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Elektrochemiczne narzędzia diagnostyczne w pomiarach gazowego nadtlenku wodoru

Electrochemical diagnostic systems for measurement of gaseous
hydrogen peroxide

Praca doktorska wykonana
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Podziękowania

Składam serdeczne podziękowania mojemu Promotorowi,
dr. hab. Dariuszowi Guziejewskiemu, prof. UŁ,
za opiekę naukową, cenne uwagi i sugestie,
a także za okazaną pomoc, wsparcie oraz poświęcony czas
podczas realizacji niniejszej rozprawy doktorskiej.

Pragnę złożyć podziękowania **dr. Valentinowi Mirceskiemu, prof. UŁ**
za wsparcie merytoryczne, cenne wskazówki oraz wartościowe
dyskusje naukowe, które przyczyniły się do powstania niniejszej dysertacji.

Dziękuję również **dr. Nabiemu Ullahowi** za życzliwość,
codzienną współpracę oraz inspirujące rozmowy i wymianę doświadczeń,
które towarzyszyły mi przez cały okres pracy naukowej.

Chciałbym również podziękować **pracownikom i doktorantom**
Zakładu Analizy Instrumentalnej za życzliwość,
okazaną pomoc i przyjazną atmosferę.

Na koniec chciałbym podziękować moim **Rodzicom** oraz **Bratu**
za wsparcie, cierpliwość i wiarę we mnie,
a przede wszystkim za to, że zawsze mogłem na Was liczyć.

Spis publikacji stanowiących podstawę niniejszej rozprawy doktorskiej:

- N. Ullah, D. Guziejewski, B. Barton, V. Mirceski, Electrocatalytic reduction of hydrogen peroxide in solution in the presence of polyacrylic acid and copper ions: Application for gaseous hydrogen peroxide detection, *Journal of Electroanalytical Chemistry*, 951 (2023) 117918.
- B. Barton, N. Ullah, D. Guziejewski, P. Krzyczmonik, V. Jovanovski, V. Mirceski, Detection of gaseous hydrogen peroxide using polyacrylic acid–copper(II) catalytic system at carbon-based screen-printed electrodes, *Ionics*, 31 (2025) 12245-12256.
- B. Barton, N. Ullah, V. Mirceski, S. Smarzewska, K. Koszelska, V. Jovanovski, D. Guziejewski, Polyelectrolyte-Enhanced Electrochemical Sensing of Gaseous Hydrogen Peroxide With Copper(II)–Mediating Systems, *Electroanalysis*, 38 (2026) e70113.
- B. Barton, N. Ullah, V. Mirceski, D. Guziejewski Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface; in *Microchemical Journal* (w recenzji w czasopiśmie *Microchemical Journal*)

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Wykaz skrótów

CV – woltamperometria cykliczna

SWV – woltamperometria fali prostokątnej

DSWV – różnicowa woltamperometria fali prostokątnej

EFS – elektrochemiczna spektroskopia faradajowska

TPB – granica trzech faz

PAA – kwas poliakrylowy

pAMPS – kwas poli(2-akrylamido-2-metylo-1-propanosulfonowy)

pAAmAA – kopolimer poli(akrylamidu-co-kwasu akrylowego)

SPE – elektroda sitodrukowana

PB – błękit pruski

PW – biel pruska

PB-SPE – elektroda sitodrukowana modyfikowana błękitem pruskim

CoPC – ftalocyjanina kobaltu(II)

CoPC-SPE – elektroda sitodrukowana modyfikowana ftalocyjaniną kobaltu(II)

GCE – dyskowa elektroda z węgla szklistego

GCER – prętowa elektroda z węgla szklistego

PIGE – elektroda grafitowa impregnowana parafiną

TATP – triacetonotriperoksyd

HMTD – heksametylenotriperoksydiamina

CL – chemiluminescencja

HRP/BSA – peroksydaza chrzanowa/albumina surowicy bydlęcej

PhC – kryształ fotoniczny

Streszczenie

Nadtlenek wodoru należy do grupy reaktywnych form tlenu i odgrywa istotną rolę w wielu procesach biologicznych oraz chemicznych. W organizmie człowieka uczestniczy między innymi w procesach biosyntezy, przekazywaniu i regulacji sygnałów komórkowych, a także w mechanizmach odpowiedzi immunologicznej. Jednocześnie jego nadmierna akumulacja i podwyższone stężenie w wydychanym powietrzu mogą świadczyć o zaburzeniu prawidłowego funkcjonowania organizmu i stanowić potencjalny wskaźnik wielu chorób, w tym astmy i raka płuc. Z tego też względu dokładna kontrola jego stężenia w fazie gazowej stanowi bardzo ważny element współczesnej diagnostyki oraz analizy środowiska.

Niniejsza rozprawa doktorska poświęcona jest opracowaniu nowych elektrochemicznych metod detekcji gazowego nadtlenku wodoru oraz określeniu czynników wpływających na właściwości analityczne projektowanych układów pomiarowych. Badania obejmowały poznanie mechanizmów procesów elektrodowych zachodzących podczas elektrochemicznej redukcji nadtlenku wodoru w obecności elektrokatalizatora w postaci jonów miedzi(II), ocenę możliwości wykorzystania elektrod sitodrukowanych wraz z modyfikatorami ich powierzchni aktywnej oraz określenie wpływu składu elektrolitu podstawowego na właściwości analityczne opracowanych sensorów. Kluczowym elementem pracy było również opracowanie układu pomiarowego wykorzystującego granicę trzech faz oraz zastosowanie zaawansowanych technik elektrochemicznych w celu zwiększenia czułości i poprawy parametrów detekcyjnych.

Przeprowadzone badania doprowadziły do opracowania nowych strategii oznaczania gazowego nadtlenku wodoru, charakteryzujących się wysoką czułością, dobrą powtarzalnością oraz możliwością prowadzenia pomiarów w czasie rzeczywistym. Uzyskane w niniejszej pracy wyniki pozwoliły na lepsze poznanie mechanizmów elektrochemicznej redukcji nadtlenku wodoru oraz wskazały nowe rozwiązania, które mogą znaleźć zastosowanie w konstrukcji wysoko czułych sensorów gazowych.

Abstract

Hydrogen peroxide is one of the most important reactive oxygen species and plays a significant role in numerous biological and chemical processes. In the human body, it participates in biosynthesis processes, cellular signaling, and immune defense mechanisms. However, excessive accumulation of hydrogen peroxide and its elevated concentration in exhaled breath have been associated with impaired physiological function and may serve as potential biomarkers of various diseases, including asthma and lung cancer. Therefore, the accurate determination of gaseous hydrogen peroxide is of considerable importance for modern medical diagnostics and environmental monitoring.

This Ph.D. dissertation focuses on the development of new electrochemical methods for the detection of gaseous hydrogen peroxide and the investigation of factors influencing the analytical performance of the proposed sensing systems. The research involved the elucidation of electrode processes associated with the electrochemical reduction of hydrogen peroxide in the presence of copper(II) ions acting as an electrocatalyst, evaluation of the applicability of screen-printed electrodes and surface modification strategies, as well as investigation of the influence of the supporting electrolyte composition on the analytical properties of the developed sensors. A key element of the work was also the development of a measuring system based on the three-phase boundary concept and the implementation of advanced electrochemical techniques to further improve sensitivity and analytical performance.

The conducted research led to the development of new strategies for the determination of gaseous hydrogen peroxide, offering high sensitivity, good repeatability, and the capability for real-time measurements. The findings presented in this dissertation contributed to a better understanding of the mechanisms of electrochemical hydrogen peroxide reduction and provided new approaches that may be applied in the design of highly sensitive gas sensors.

Autoreferat

Wprowadzenie

Związek pomiędzy nadtlenkiem wodoru a procesami życia ma charakter złożony, wielowymiarowy i dynamiczny. Przez długi czas nadtlenek wodoru postrzegany był przede wszystkim jako toksyczny produkt uboczny przemian tlenowych, odpowiedzialny za uszkodzenia struktur komórkowych oraz zaburzenia funkcjonowania organizmów. Taki obraz wynikał głównie z jego zdolności do generowania reaktywnych form tlenu oraz udziału w procesach prowadzących do degradacji biomolekuł. Dopiero rozwój badań nad reaktywnymi formami tlenu oraz mechanizmami regulacji redoks pozwolił na zmianę tego podejścia, gdzie wykazano, że rola nadtlenku wodoru w układach biologicznych jest znacznie bardziej złożona niż wcześniej przypuszczano [1].

Obecnie wiadomo, że metabolicznie wytwarzany nadtlenek wodoru odgrywa istotną rolę w regulacji procesów komórkowych, pełniąc funkcję cząsteczki sygnałowej w układach redoks. Uczestniczy on w mechanizmach związanych z proliferacją komórek, ich różnicowaniem, starzeniem się oraz procesami apoptozy [2, 3], a także bierze udział w odpowiedzi immunologicznej organizmu, wpływając na mechanizmy obronne przeciwko patogenom oraz regulując przebieg procesów zapalnych [4, 5]. Tym samym nadtlenek wodoru przestał być postrzegany wyłącznie jako czynnik uszkodzający, a zaczął być traktowany jako integralny element funkcjonowania układów biologicznych.

Źródłem nadtlenku wodoru w organizmach tlenowych są głównie procesy związane z metabolizmem tlenu. Podczas przemian zachodzących w mitochondrialnym łańcuchu oddechowym cząsteczkowy tlen pełni rolę końcowego akceptora elektronów, ulegając przy tym czteroelektronowej redukcji do wody. W jej trakcie następuje akumulacja reaktywnych form tlenu, które można podzielić na bardzo niestabilne i wysoce reaktywne, takie jak rodniki hydroksylowe, które mogą prowadzić do generowania reaktywnych aldehydów i śmierci komórek oraz wykazujące większą stabilność i mniejszą reaktywność, jak nadtlenek wodoru, który następnie może zostać wykorzystany jako wewnątrzkomórkowy przekaźnik. Z chemicznego punktu widzenia nadtlenek wodoru jest umiarkowanie reaktywnym utleniaczem, jednak jego rzeczywista aktywność w układach biologicznych wynika przede wszystkim z możliwości generowania bardziej reaktywnych form tlenu, co głównie jest możliwe poprzez reakcję Fentona. Obecność jonów Fe^{2+} czy Cu^+ oraz nadtlenku wodoru prowadzi do powstawania rodników hydroksylowych, co bezpośrednio wiąże się z ryzykiem wystąpienia stresu oksydacyjnego [6]. Zjawiska te podkreślają dualny charakter nadtlenku wodoru, który z jednej strony jest niezbędny dla prawidłowego

funkcjonowania organizmów, z drugiej natomiast może stanowić źródło uszkodzeń na poziomie molekularnym.

Poza swoim znaczeniem biologicznym nadtlenek wodoru znajduje bardzo szerokie zastosowanie w różnych gałęziach przemysłu, co wynika przede wszystkim z jego silnych właściwości utleniających oraz stosunkowo prostego i bezpiecznego dla środowiska mechanizmu rozkładu do wody i tlenu. Dzięki tym właściwościom jest on często traktowany jako bezpieczniejsza alternatywa dla bardziej agresywnych i mniej przyjaznych środowisku utleniaczy, jak na przykład związki chloru [7]. W praktyce oznacza to, że może być wykorzystywany w procesach, gdzie duże znaczenie ma jednocześnie zachowanie wysokiej efektywności utleniania jak i ograniczenie powstawania toksycznych produktów ubocznych. Z tego też powodu, jednym z głównych obszarów zastosowania nadtlenu wodoru jest przemysł spożywczy [8]. Jego zdolność do generowania reaktywnych form tlenu sprawia, iż wykazuje on silne działanie przeciwdrobnoustrojowe działając tym samym jako świetny środek dezynfekujący i odkażający powierzchnie produkcyjne, urządzenia oraz opakowania żywności [9]. Mechanizm jego działania polega przede wszystkim na utlenianiu wielu związków obecnych w komórkach, takich jak białka czy DNA, w konsekwencji prowadząc do śmierci drobnoustrojów [7, 10]. Właściwości dezynfekujące nadtlenu wodoru znalazły również zastosowanie w technologiach uzdatniania wody, gdzie jest stosowany jako środek do wspomagania eliminacji patogennych mikroorganizmów, takich jak bakterie, wirusy i pierwotniaki. Dodatkowo, odgrywa on kluczową rolę w zaawansowanych procesach utleniania, umożliwiając tym samym rozkład trwałych zanieczyszczeń organicznych [11].

Innym obszarem, w którym nadtlenek wodoru znajduje zastosowanie jest przemysł farmaceutyczny i medyczny. W tym przypadku, jego rola nie ogranicza się wyłącznie do działania dezynfekującego, lecz obejmuje ona między innymi udział w procesach gojenia ran, gdzie wspomaga eliminację drobnoustrojów oraz pełni funkcję cząsteczki sygnałowej wysyłając informację o uszkodzeniu. Niemniej jednak, biologiczne działanie nadtlenu wodoru jest silnie zależne od jego stężenia. W wyższych stężeniach wykazuje on silne właściwości prozapalne oraz utleniające, przyczyniające się do efektu dezynfekującego, natomiast w niższych stężeniach wspomaga procesy regeneracyjne [12, 13].

Istotne znaczenie nadtlenu wodoru ma również w przemyśle tekstylnym oraz papierniczym, gdzie wykorzystywany jest głównie jako środek wybielający. W procesach tych odpowiada za utlenianie barwników oraz innych zanieczyszczeń organicznych

obecnych w surowcach, co pozwala na uzyskanie produktów o jednolitej barwie oraz poprawionych właściwościach użytkowych [14].

Szerokie zastosowania nadtlenu wodoru zamyka przemysł paliwowy, w którym coraz częściej pojawia się on jako alternatywny utleniacz zastępujący tlen. Jego wykorzystanie w tego typu układach wynika przede wszystkim z możliwości pracy w środowiskach beztlenowych, takich jak przestrzeń kosmiczna czy środowisko podwodne, w których obecność tlenu wymaga dodatkowego zbiornika w systemie. Ponadto, zastosowanie nadtlenu wodoru jako utleniacza może prowadzić do zwiększenia teoretycznego napięcia ogniwa, a tym samym poprawy wydajności konwersji energii. Korzystnym aspektem jest również stosunkowo niska strata aktywacyjna reakcji redukcji nadtlenu wodoru, wynikająca z dwuelektronowego transferu elektronów [15, 16].

Pomimo szerokiego zastosowania technologicznego, znaczenie nadtlenu wodoru w kontekście organizmu człowieka pozostaje szczególnie ważne. Jak już wcześniej wspomniano, wykazuje on charakter dualny i jego rola przede wszystkim zależy od lokalnego stężenia oraz warunków środowiska komórkowego [4]. W prawidłowych warunkach bierze on udział w procesach komunikacji molekularnej oraz w mechanizmach obrony organizmu przed patogenami. Nadtlenek wodoru powstaje na skutek dysmutacji anionorodnika ponadtlenkowego, a następnie może dyfundować przez błony komórkowe, umożliwiając przekazywanie sygnału pomiędzy różnymi obszarami komórki. W procesach tych uczestniczy w regulacji aktywności licznych czynników transkrypcyjnych oraz szlaków metabolicznych, co bezpośrednio przekłada się na odpowiedź komórki na bodźce zewnętrzne [17]. Jednocześnie jak zostało wcześniej podkreślone, nadmierna akumulacja nadtlenu wodoru prowadzi do zaburzenia równowagi redoks i w konsekwencji do wystąpienia stresu oksydacyjnego. Koncepcja biologicznego stresu oksydacyjnego została opisana szczegółowo przez Helmuta Siesa [18] i zdefiniowana jako „brak równowagi między utleniaczami i przeciwutleniaczami na korzyść utleniaczy, prowadzący do zakłócenia sygnalizacji i kontroli redoks i/lub uszkodzenia molekularnego” [19]. W praktyce oznacza to, iż powstałe w wyniku nadprodukcji reaktywne formy tlenu mogą oddziaływać z podstawowymi składnikami komórki, takimi jak białka, lipidy czy kwasy nukleinowe, prowadząc do zaburzenia ich struktury i funkcji [20, 21]. Liczne badania wykazały, że stres oksydacyjny odgrywa znaczącą rolę w patogenezie wielu chorób, w tym nowotworów złośliwych, chorób neurodegeneracyjnych, tj. chorobie Alzheimera czy Parkinsona, a także schorzeń układu oddechowego i sercowo-naczyniowego [4, 17, 20, 22-26].

W związku z obserwowanymi zależnościami nadtlenu wodoru uznawany jest za jeden z najbardziej reprezentatywnych wskaźników stresu oksydacyjnego. Wynika to między innymi z faktu, że oszacowanie wielu klasycznych parametrów opisujących ten stan jest stosunkowo złożone i wymaga wykorzystania zaawansowanej aparatury, takiej jak spektroskopia elektronowego rezonansu spinowego czy wysokosprawna chromatografia cieczowa, a uzyskiwane w ten sposób wyniki nie zawsze cechują się wysoką swoistością [26]. Na tym tle nadtlenu wodoru stanowi bardziej bezpośredni wskaźnik zmian zachodzących w organizmie, ponieważ jest on zarówno produktem przemian metabolicznych, jak i aktywnym uczestnikiem procesów sygnałowych. W związku z tym, jego obecność w płynach ustrojowych może odzwierciedlać aktualny stan równowagi redoks, jednocześnie dostarczając informacji o rozwijających się stanach patologicznych. Ponadto, warto zaznaczyć, że nadtlenu wodoru powstaje również jako produkt reakcji enzymatycznych katalizowanych przez oksydazy, sprawiając, iż jego oznaczanie może dostarczać informacji o przebiegu tych procesów bez konieczności bezpośredniego oznaczania samych substratów [27].

W efekcie dokładna detekcja nadtlenu wodoru pozostaje przedmiotem dużego zainteresowania w literaturze. W ostatnich latach szczególne znaczenie zyskuje oznaczanie nadtlenu wodoru w fazie gazowej, zwłaszcza w wydychanym powietrzu [28-30]. Analiza składu oddechu jest nieinwazyjną metodą diagnostyczną, która umożliwia uzyskanie informacji o stanie fizjologicznym organizmu bez konieczności pobierania próbek biologicznych w sposób ingerujący w organizm pacjenta [31]. Wydychane powietrze stanowi złożoną mieszaninę gazów, zawierającą oprócz głównych składników, czyli azotu, tlenu czy dwutlenku węgla, również liczne związki lotne obecne w bardzo niskich stężeniach, sięgających nawet ppt [32]. Wśród nich znajdują się zarówno lotne związki organiczne, jak i nieorganiczne produkty przemian metabolicznych, w tym właśnie nadtlenu wodoru. W przypadku zaburzeń układu oddechowego, takich jak astma, rak płuc czy przewlekła obturacyjna choroba płuc, obserwuje się zwiększoną produkcję reaktywnych form tlenu przez makrofagi i neutrofile, co w konsekwencji prowadzi do podwyższonego stężenia nadtlenu wodoru w wydychanym powietrzu [33]. Stwarza to możliwość wykorzystania oznaczania nadtlenu wodoru w diagnostyce oraz monitorowaniu przebiegu tych chorób. Należy jednak zaznaczyć, że dokładny pomiar nadtlenu wodoru w fazie gazowej jest trudny do przeprowadzenia, głównie ze względu na jego niskie stężenie, zdolność do łatwego utleniania na powietrzu oraz obecność w matrycy gazowej licznych substancji zakłócających.

Oznaczanie nadtlenu wodoru w fazie gazowej ma znaczenie nie tylko w kontekście diagnostyki medycznej, ale również w obszarze bezpieczeństwa publicznego. Nadtlenek wodoru jest jednym z kluczowych prekursorów stosowanych w syntezie nadtlenkowych materiałów wybuchowych, do których należą między innymi triacetonotriperoksyd (TATP) czy heksametylenotriperoksydiamina (HMTD). Związki te mogą być otrzymywane stosunkowo prostymi metodami z wykorzystaniem łatwo dostępnych w handlu reagentów, polegającymi na reakcji nadtlenkowego prekursora z acetonem w środowisku kwaśnym, co niestety przekłada się na częste ich wykorzystanie w improwizowanych i „domowych” ładunkach wybuchowych [34]. Istotnym problemem związanym z tymi substancjami jest ich wysoka niestabilność oraz brak klasycznych grup funkcyjnych, w szczególności grup nitrowych, charakterystycznych dla większości tradycyjnych materiałów wybuchowych. W konsekwencji ich bezpośrednia detekcja jest utrudniona, a stosowane metody analityczne wymagają często złożonej aparatury oraz odpowiedniego przygotowania próbki [35, 36]. Dodatkowo, zarówno w trakcie syntezy, jak i rozkładu tych związków może dochodzić do uwalniania nadtlenu wodoru do otoczenia, w tym do fazy gazowej [35]. Oznacza to, że monitorowanie poziomu nadtlenu wodoru w powietrzu może stanowić pośredni wskaźnik obecności samych materiałów wybuchowych. To podejście staje się kluczowe w sytuacjach, w których bezpośrednia identyfikacja materiałów wybuchowych nie jest możliwa, na przykład w przypadku śladowych ilości substancji lub próbek zdegradowanych.

W celu detekcji nadtlenu wodoru opracowano szereg metod analitycznych obejmujących techniki spektroskopowe, luminescencyjne czy elektrochemiczne. Do najczęściej stosowanych należą między innymi spektrofotometria [37], fluorescencja [38, 39], chemiluminescencja [40], kolorymetria [41] oraz metody chromatograficzne, w tym wysokosprawna chromatografia cieczowa [42]. W literaturze opisywane są również bardziej zaawansowane podejścia analityczne wykorzystujące sprzężone techniki chromatograficzne z detekcją mas (GC-MS/HPLC-MS) [43, 44] oraz metody spektroskopowe takie jak spektroskopia w podczerwieni oraz spektroskopia Ramana [45]. Szczególne znaczenie w analizie śladowych ilości nadtlenu wodoru mają techniki luminescencyjne, zwłaszcza chemiluminescencja, która dzięki bardzo niskiemu poziomowi sygnału tła umożliwia osiągnięcie niskich granic oznaczalności. Natomiast techniki chromatograficzne sprzężone z detekcją mas pozwalają nie tylko na ilościowe oznaczanie analitu, lecz również na identyfikację poszczególnych składników próbki, co ma istotne znaczenie dla analiz w złożonych matrycach środowiskowych i biologicznych. Niektóre

z powyższych procedur analitycznych zostały przystosowane do detekcji nie tylko ciekłego, ale również gazowego nadtlenu wodoru. Do tego celu wykorzystywane są między innymi techniki bazujące na spektrometrii mas [46, 47], chemiluminescencji [48, 49], spektrofotometrii UV-Vis [37, 50, 51], spektrofluorymetrii [52] oraz sensorach amperometrycznych [53].

Wszystkie wymienione techniki charakteryzują się wysoką czułością oraz możliwością oznaczania bardzo niskich stężeń analitu, niemniej jednak, ich zastosowanie często wiąże się z pewnymi ograniczeniami. W przypadku technik spektrofotometrycznych bezpośrednia detekcja nadtlenu wodoru nie jest możliwa, co wynika z braku charakterystyki emisyjnej i absorpcyjnej zarówno w zakresie widzialnym, jak i ultrafioletowym [54]. Problem ten rozwiązano poprzez zastosowanie dodatkowych reagentów w postaci wskaźników redoks, które ulegają przemianom prowadzącym do zmiany barwy. Podejście to znalazło szerokie zastosowanie w analizie próbek ciekłych, jednakże jego wykorzystanie w przypadku fazy gazowej pozostaje nadal słabo zbadane [37]. Z kolei, zaawansowane techniki instrumentalne bazujące na chromatografii, mimo bardzo wysokiej dokładności, wymagają kosztownej aparatury, odpowiedniego przygotowania próbki, a także wykwalifikowanej obsługi, co w praktyce w dużym stopniu ogranicza ich dostępność w wielu laboratoriach oraz utrudnia ich zastosowanie w analizach terenowych i pomiarach prowadzonych w czasie rzeczywistym. Ponadto, dodatkowym utrudnieniem w przypadku analizy gazowego nadtlenu wodoru jest konieczność efektywnego przeniesienia jego próbki do układu pomiarowego przy jednoczesnym zachowaniu jego stabilności. Problem ten jest szczególnie istotny podczas analiz prowadzonych w czasie rzeczywistym, gdzie niezwykle ważny jest krótki czas odpowiedzi układu oraz możliwość prowadzenia bezpośrednich pomiarów bez konieczności wieloetapowego przygotowania próbki.

W odpowiedzi na powyższe ograniczenia coraz większe zainteresowanie zyskują metody elektrochemiczne [55-58]. Zasada działania technik elektrochemicznych opiera się na pomiarze zmian prądu, potencjału lub oporu (przewodnictwa), związanych z procesami utleniania i redukcji analitu. W zależności od zastosowanej techniki pomiarowej wyróżnia się między innymi techniki amperometryczne, potencjometryczne, konduktometryczne oraz woltamperometryczne [59]. Szczególnie szerokie zastosowanie znajdują te ostatnie, w których to rejestrowana jest zależność natężenia prądu od przyłożonego potencjału, co pozwala zarówno na jakościowe, jak i ilościowe oznaczanie badanej substancji. Procesy elektrochemiczne zachodzą na granicy faz elektroda-elektrolit i polegają na wymuszonej

różnicą potencjałów wymianie elektronów pomiędzy elektrodą a cząsteczkami analitu. W wyniku tych przemian generowany jest sygnał elektryczny, którego charakter oraz intensywność zależą od stężenia oznaczanej substancji, kinetyki reakcji elektrochemicznej, transportu masy oraz zjawisk zachodzących na powierzchni elektrody [60].

Metody elektrochemiczne wyróżniają się wysoką czułością, krótkim czasem odpowiedzi oraz stosunkowo niedrogą aparaturą. Dodatkowo, metody te sprzyjają miniaturyzacji układów pomiarowych oraz prowadzeniu analiz w czasie rzeczywistym, co czyni je atrakcyjnymi w zastosowaniach środowiskowych i medycznych. Na szczególną uwagę zasługuje również możliwość modyfikacji powierzchni elektrod, pozwalająca na dostosowywanie ich właściwości do oznaczania konkretnych analitów, a tym samym poprawę selektywności oraz czułości detekcji [59]. W kontekście oznaczania nadtlenu wodoru metody elektrochemiczne stają się tym bardziej atrakcyjne, gdyż związek ten wykazuje wyraźne właściwości redoks mogące uczestniczyć zarówno w reakcjach utleniania, jak i redukcji, co wynika z jego termodynamicznej niestabilności [61]. Zjawisko to umożliwia jego detekcję w oparciu o oba kierunki przemian elektrochemicznych, co stanowi znaczącą przewagę nad wieloma innymi technikami analitycznymi. Pozwala to również na świadomy dobór mechanizmu detekcji poprzez wybór odpowiedniego procesu elektrodowego i dostosowanie właściwości elektrody, na przykład poprzez zastosowanie odpowiednich materiałów katalitycznych lub modyfikatorów powierzchni, które będą wspomagać dany proces elektrochemiczny zwiększając tym samym czułość i selektywność analizy. Co więcej, w elektroanalizie nadtlenu wodoru kluczową rolę odgrywają procesy elektrokatalityczne, umożliwiające obniżenie nadpotencjału reakcji elektrodowej oraz poprawę możliwości analitycznych układu [62]. Dlatego też, liczne badania skupiają się na rozwijaniu układów wykorzystujących materiały węglowe, nanomateriały, układy kompozytowe czy metale przejściowe, które mogą pełnić funkcję aktywnych mediatorów redoks pośredniczących w transferze elektronów pomiędzy analitem a elektrodą pracującą. Podejście to pozwala na zwiększenie szybkości reakcji elektrodowej, poprawę efektywności przemian redoks nadtlenu wodoru oraz ograniczenie wpływu wysokich wartości potencjałów, co przekłada się na poprawę stabilności i czułości uzyskiwanego sygnału analitycznego. Wśród tego typu rozwiązań uwagę zwracają układy oparte na jonach miedzi(II), zdolne do uczestniczenia w odwracalnych przemianach redoks oraz inicjowania procesów elektrokatalitycznych związanych z redukcją i utlenianiem nadtlenu wodoru [63].

Niemniej jednak, pomimo intensywnego rozwoju elektrochemicznych metod oznaczania nadtlenu wodoru, zdecydowana większość opisanych w literaturze rozwiązań dotyczy analiz prowadzonych w fazie ciekłej [64, 65]. W konsekwencji stan wiedzy w zakresie elektrochemicznej detekcji w fazie gazowej pozostaje niewystarczający. Odnosi się to zarówno do ograniczonej liczby opracowanych układów pomiarowych, jak i do niepełnego poznania mechanizmów oraz czynników kształtujących ich parametry analityczne. Warto zaznaczyć, że w literaturze niewiele uwagi poświęcono wpływowi składu elektrolitu podstawowego, procesów elektrokatalitycznych oraz transportu masy na przebieg detekcji gazowego nadtlenu wodoru. Zatem, dostępnych układów detekcyjnych nadtlenu wodoru w fazie gazowej jest nadal stosunkowo niewiele, zwłaszcza w odniesieniu do metod umożliwiających prowadzenie szybkich i dokładnych pomiarów *in situ*. Dodatkowo, wiele z obecnie dostępnych rozwiązań często wymaga stosowania skomplikowanych układów pomiarowych, specjalistycznych materiałów lub wieloetapowego przygotowania próbki bądź systemu detekcyjnego, co może utrudniać ich praktyczne zastosowanie w szybkich analizach w czasie rzeczywistym. Staje się to szczególnie problematyczne w przypadku badań w złożonych matrycach gazowych zawierających między innymi tlen czy parę wodną, które w znaczący sposób mogą wpływać na przebieg procesów elektrodowych i stabilność uzyskiwanego sygnału analitycznego. Ponadto, ważnym aspektem w tym temacie, a wymagającym dalszych badań jest rola układów elektrokatalitycznych. Pomimo licznych doniesień o wykorzystaniu jonów metali przejściowych i innych materiałów wspomagających zachodzenie reakcji w oznaczaniu ciekłego nadtlenu wodoru, ich zastosowanie w analizie gazowej pozostaje słabo rozpoznane. Jednocześnie niewiele danych literaturowych porusza temat wykorzystania jonów miedzi(II) jako mediatorów procesów elektrokatalitycznych podczas elektrochemicznej detekcji gazowego nadtlenu wodoru. Podobnie nieliczne prace poświęcone są wykorzystaniu zaawansowanych technik woltamperometrycznych oraz alternatywnych konfiguracji pomiarowych, takich jak układ trójfazowy, w celu poprawy parametrów analitycznych układów przeznaczonych do detekcji gazowego nadtlenu wodoru. Bezpośrednio związanym z tym zagadnieniem pozostaje zapewnienie efektywnego transportu gazowego analitu do powierzchni elektrody przy jednoczesnym zachowaniu wysokiej czułości i powtarzalności pomiarów.

Podsumowując, nadal istnieje potrzeba opracowania nowych układów elektroanalitycznych umożliwiających bezpośrednią, czułą oraz wiarygodną detekcję nadtlenu wodoru w fazie gazowej. Niniejsza dysertacja stanowi odpowiedź na niedostatek

kompleksowych badań dotyczących elektrochemicznej detekcji gazowego nadtlenu wodoru, obejmujących jednoczesną optymalizację składu elektrolitu podstawowego, materiału elektrodowego, układów elektrokatalitycznych oraz konfiguracji pomiarowej. Przyjęto, że odpowiedni dobór tych parametrów, w połączeniu z wykorzystaniem jonów miedzi(II) jako mediatorów procesów elektrokatalitycznych oraz zastosowaniem zaawansowanych technik elektroanalitycznych, umożliwi opracowanie czułych i powtarzalnych metod oznaczania nadtlenu wodoru w fazie gazowej.

Tematyka i cel badań

Tematyka niniejszej dysertacji obejmuje badania nad elektrochemiczną detekcją nadtlenu wodoru w fazie gazowej oraz opracowanie układów pomiarowych umożliwiających jego oznaczanie bezpośrednio w miejscu występowania. Głównym celem pracy było stworzenie przenośnych, szybkich, precyzyjnych oraz niezawodnych metod elektrochemicznej detekcji gazowego nadtlenu wodoru z wykorzystaniem układów elektrokatalitycznych opartych na jonach miedzi(II).

Realizacja założonego celu została podzielona na kilka etapów badawczych. W pierwszym etapie skupiono się na badaniu procesów elektrochemicznych związanych z oznaczaniem gazowego nadtlenu wodoru z wykorzystaniem układów zawierających jony miedzi(II), pełniących funkcję elektrokatalizatora. Następny etap badań obejmował optymalizację składu elektrolitu podstawowego poprzez analizę wpływu wybranych polielektrolitów na możliwości detekcji nadtlenu wodoru w fazie gazowej. Równolegle analizowane były możliwości miniaturyzacji układu pomiarowego z wykorzystaniem elektrod sitodrukowanych oraz wpływ modyfikatorów ich powierzchni roboczej na czułość i powtarzalność uzyskiwanego sygnału analitycznego. Trzeci etap obejmował opracowanie oraz zastosowanie nowatorskiego układu pomiarowego opartego na prowadzeniu badań z wykorzystaniem granicy trzech faz: ciekłej, stałej i gazowej. Ostatni etap pracy zakładał zastosowanie nowoczesnych technik elektroanalitycznych, w tym różnicowej woltamperometrii fali prostokątnej (DSWV) oraz elektrochemicznej spektroskopii faradajowskiej (EFS), w celu dalszej optymalizacji procedur pomiarowych oraz sposobu przetwarzania sygnału analitycznego.

Układ pomiarowy

Większość badań elektrochemicznych prowadziłem z wykorzystaniem potencjostatu Autolab PGSTAT 302N sterowanego oprogramowaniem NOVA (wersja 2.1.5, Metrohm-Autolab, Holandia). Część pomiarów wykonałem przy użyciu przenośnego bipotencjostatu μ Stat 200 Bipotentiostat STAT200 (Metrohm DropSens, Hiszpania) pracującego z programem DropView.

W trakcie badań zależnie od charakteru prowadzonych eksperymentów stosowałem kilka konfiguracji elektrodowych:

- klasyczny układ trójelektrodowy składający się z dyskowej elektrody roboczej z węgla szklatego (GCE), elektrody odniesienia Ag/AgCl (3 mol L⁻¹ KCl) oraz elektrody pomocniczej w postaci drutu platynowego
- elektrod sitodrukowanych (SPE) (DropSens, Hiszpania):
 - niezmodyfikowanej węglowej elektrody sitodrukowanej nr ref. 110;
 - niezmodyfikowanej węglowej elektrody sitodrukowanej nr ref. C110;
 - węglowej elektrody sitodrukowanej modyfikowanej ftalocyjaniną kobaltu(II) nr ref. 410;
 - węglowej elektrody sitodrukowanej modyfikowanej błękitem pruskim nr ref. 710.

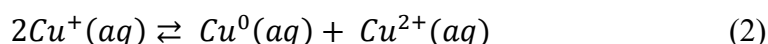
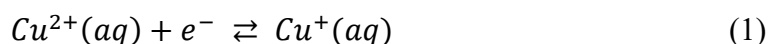
Wszystkie wykorzystane elektrody sitodrukowane składały się z węglowej elektrody roboczej, srebrnej elektrody quasi-odniesienia oraz węglowej elektrody pomocniczej.

- układ do detekcji trójfazowej, w którym wykorzystałem elektrodę odniesienia Ag/AgCl (3 mol L⁻¹ KCl), drut platynowy jako elektrodę pomocniczą, a także elektrody pracujące:
 - prętową elektrodę z węgla szklatego (GCER);
 - elektrodę grafitową impregnowaną parafiną (PIGE);
 - siatkę miedzianą;
 - siatkę złotą;
 - drut złoty;
 - drut platynowy.

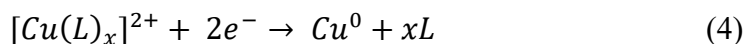
Wszystkie użyte przeze mnie odczynniki były czystości co najmniej analitycznej i były stosowane bez dodatkowego oczyszczania. Wykorzystywana woda dejonizowana pochodziła z systemu oczyszczania wody Polwater DL-3 (Polwater, Polska).

Podsumowanie badań własnych

Punktem wyjścia do realizacji badań w temacie niniejszej dysertacji były wcześniejsze doniesienia literaturowe dotyczące elektrochemii jonów miedzi(II) w środowisku kwasu poliakrylowego (PAA) [66]. Autorzy wykazali w nich, że obecność polielektrolitu prowadzi do istotnych zmian w przebiegu procesów redoks układu $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}^0$. Jak wiadomo, elektrochemiczna redukcja jonów Cu^{2+} w niekompleksującym środowisku wodnym przebiega dwuetapowo poprzez utworzenie jonów Cu^+ jako produktu pośredniego (równania 1 i 3). Powstające jony Cu^+ są jednak termodynamicznie niestabilne i ulegają szybkiej reakcji dysproporcjonowania (równanie 2), co ogranicza ich udział w dalszych przemianach elektrochemicznych.



Natomiast w obecności ligandów kompleksujących przebieg procesów redoks miedzi może ulegać znacznym zmianom, a ponadto możliwe staje się występowanie redukcji tych kompleksów zgodnie z równaniem 4. Wspomniana praca wykazała, iż obecność PAA prowadzi do stabilizacji pośrednich jonów Cu^+ , wpływając na równowagę pomiędzy poszczególnymi formami miedzi obecnymi w układzie. W następstwie, zjawisko to stwarzało możliwość skuteczniejszego wykorzystania pary redoks $\text{Cu}^{2+}/\text{Cu}^+$ w procesach elektrokatalitycznych związanych z przemianami nadtlenu wodoru.

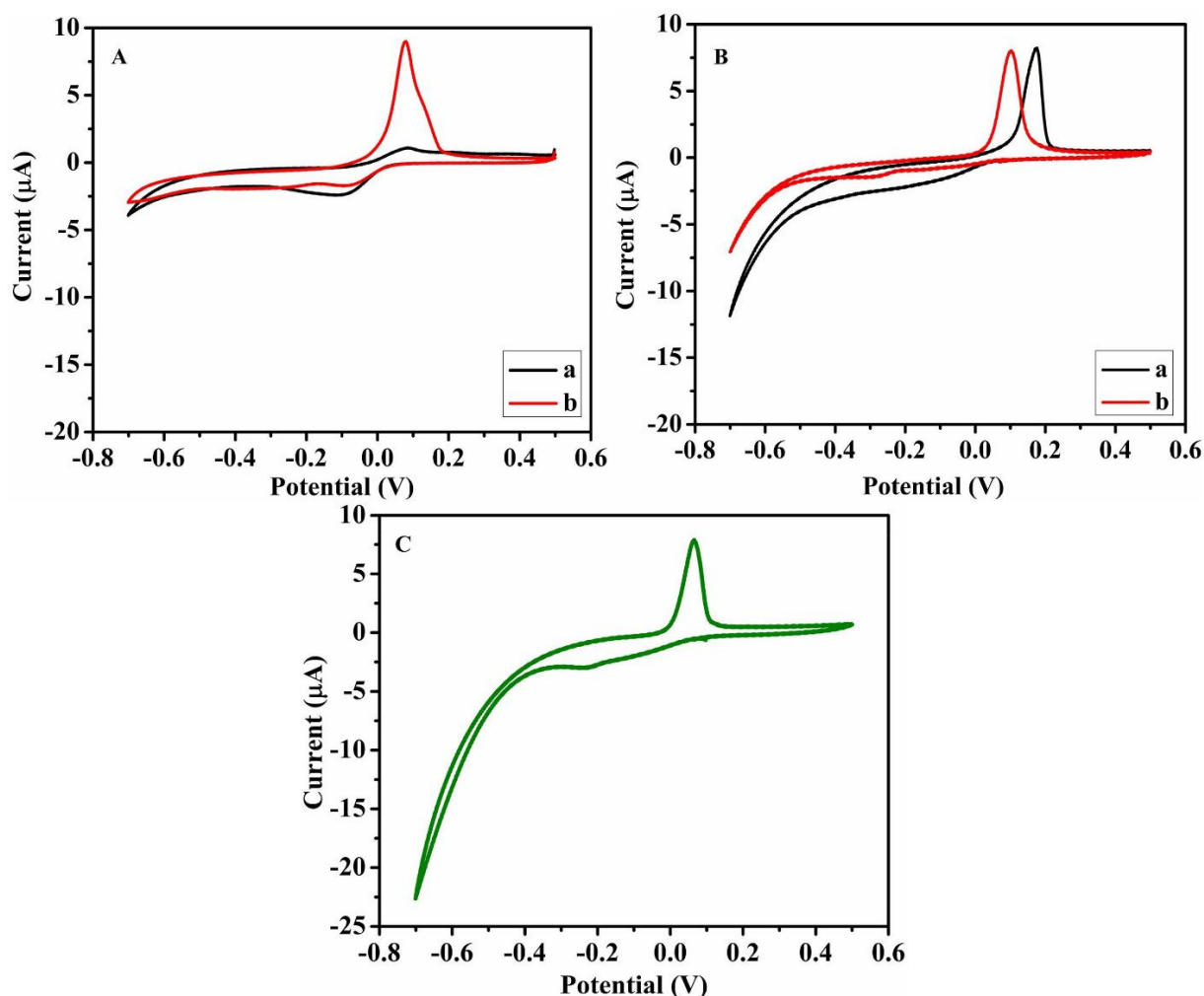


Drugą istotną zaletą PAA były wykazywane przezeń właściwości sorpcyjne oraz zdolność do tworzenia stabilnych, cienkich warstw na powierzchni elektrody [67]. Dzięki tym właściwościom mógł on pełnić jednocześnie funkcję medium akumulującego gazowy analit oraz środowiska sprzyjającego zachodzeniu procesów elektrokatalitycznych. Wskazywało to, że połączenie właściwości sorpcyjnych PAA z aktywnością redoks jonów miedzi(II) może stanowić podstawę do opracowania nowych układów przeznaczonych do detekcji gazowego nadtlenu wodoru. Zgodnie z powyższymi przesłankami podjąłem

badania nad wykorzystaniem układu PAA–Cu²⁺ w elektrochemicznej detekcji gazowego H₂O₂.

W początkowym etapie moich badań skoncentrowałem się na charakteryzacji procesów elektrokatalitycznej redukcji nadtlenu wodoru w układach zawierających jony miedzi(II) oraz kwas poliakrylowy, co stanowiło podstawę do dalszego rozwoju metod detekcji gazowego H₂O₂. Badania prowadzone z wykorzystaniem klasycznych technik woltamperometrycznych, głównie woltamperometrii cyklicznej (CV) oraz woltamperometrii fali prostokątnej (SWV), wykazały, że obecność tlenu w roztworze KNO₃ zawierającym jony Cu²⁺ wpływa na przebieg procesów elektrochemicznych zachodzących na powierzchni elektrody (Rys. 1A). Charakter uzyskiwanych sygnałów wskazywał na występowanie regeneracyjnego mechanizmu redoks typu EC', sugerując udział pośrednich jonów Cu⁺ w reakcjach z rozpuszczonym tlenem, prowadzących do formowania jonów Cu²⁺ oraz jednoczesnego powstawania nadtlenu wodoru. Obecność PAA w elektrolicie podstawowym prowadziła do wyraźnej zmiany przebiegu rejestrowanych procesów elektrochemicznych (Rys. 1B). W porównaniu do roztworu niezawierającego polielektrolitu obserwowano silniejsze efekty elektrokatalityczne oraz obserwowano wyraźny wzrost prądów katodowych przy potencjałach bardziej ujemnych niż –0.400 V, co wskazywało na rozwój dodatkowego procesu redukcji. Jednocześnie zmiana morfologii piku anodowego sugerowała oddziaływanie pomiędzy PAA a formami miedzi obecnymi w roztworze, co było zgodne z wcześniejszymi badaniami [66] wskazującymi na stabilizację pośrednich jonów Cu⁺ przez kwas poliakrylowy. W obecności tlenu efekt elektrokatalityczny obserwowany w pobliżu –0.100 V ulegał dalszemu wzmocnieniu, zachowując cechy regeneracyjnego mechanizmu EC'. Wraz z zespołem zaobserwowaliśmy również, że jednoczesna obecność tlenu oraz nadtlenu wodoru powodowała występowanie złożonych procesów redoks zachodzących zarówno na powierzchni elektrody, jak i w objętości roztworu. W toku badań potwierdzone zostały wyraźne właściwości elektrokatalityczne układu Cu²⁺/Cu⁺ w obecności nadtlenu wodoru, czego efektem był znaczny wzrost odpowiedzi prądowej w zakresie bardziej ujemnych potencjałów (Rys. 1C). Zjawisko to powiązano z powstawaniem reaktywnych form tlenu, między innymi anionorodnika ponadtlenkowego oraz rodników hydroksylowych, uczestniczących w dalszych przemianach redoks (Schemat 1). Uzyskane wyniki potwierdziły, że obecność PAA nie pełni wyłącznie funkcji medium zapewniającego przewodnictwo jonowe, lecz aktywnie wpływa na przebieg procesów elektrochemicznych poprzez stabilizację form pośrednich oraz ograniczanie ich dyfuzji w objętości roztworu.

Przeprowadzone badania pozwoliły mi lepiej zrozumieć mechanizmy odpowiedzialne za wzmacnianie odpowiedzi elektrochemicznej oraz wskazały możliwość wykorzystania układów PAA-Cu²⁺ w oznaczeniach gazowego nadtlenku wodoru.

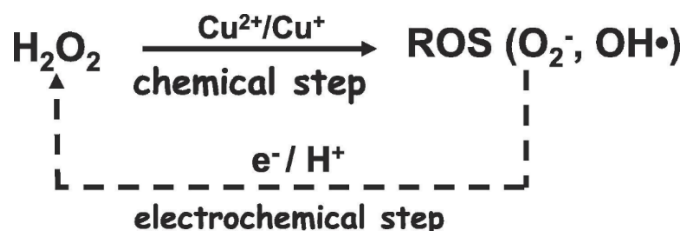


Rysunek 1. Woltamperogramy cykliczne zarejestrowane dla jonów Cu²⁺ o stężeniu 2×10^{-4} mol L⁻¹ w elektrolicie podstawowym zawierającym (A) 0.1 mol L⁻¹ KNO₃: w obecności tlenu (a) oraz po odtlenieniu roztworu (b); (B) 0.1 mol L⁻¹ KNO₃ w obecności 1% PAA, w atmosferze tlenu (a) oraz po odtlenieniu roztworu (b); (C) 0.1 mol L⁻¹ KNO₃ w obecności 1% PAA oraz 2×10^{-3} mol L⁻¹ H₂O₂ w atmosferze tlenu. Szybkość skanowania 50 mV s⁻¹. Za zgodą z artykułu [63].

Do tego celu wykorzystałem komercyjnie dostępne elektrody sitodrukowane firmy DropSens. Przed rozpoczęciem właściwych badań przeprowadziłem podstawową charakterystykę elektrochemiczną niezmodyfikowanej elektrody sitodrukowanej z wykorzystaniem układu heksacyjanożelazanu(II)/(III). Na podstawie uzyskanych wyników, korzystając z równania Randlesa-Ševčíka, wyznaczyłem współczynniki dyfuzji

oraz efektywną powierzchnię elektroaktywną elektrody, potwierdzając jednocześnie, że obecność PAA nie wpływała znacząco na właściwości dyfuzyjne związków redoks. Badania te wykazały również, że mechanizm elektrochemiczny zachodzący na powierzchni SPE pozostaje praktycznie identyczny jak w przypadku klasycznej dyskowej elektrody z węgla szklanego, co było zgodne z wcześniejszymi doniesieniami literaturowymi [66, 68]. Ostatecznie, detekcję gazowego nadtlenu wodoru wykonałem wykorzystując szczelnie zamkniętą szklaną komorę o objętości 1 L, do której wprowadzałem 50 mL wodnego roztworu H_2O_2 o określonym stężeniu (z zakresu od 1×10^{-4} do $7 \times 10^{-3} \text{ mol L}^{-1}$). Tak przygotowaną komorę z wodnym roztworem nadtlenu wodoru pozostawiałem na 3 godziny, co umożliwiało ustalenie stanu równowagi pomiędzy H_2O_2 obecnym w fazie ciekłej i gazowej oraz wysycenie atmosfery komory jego parami. Warto zaznaczyć, że czas ten został wybrany na podstawie wcześniej przeprowadzonych przeze mnie badań optymalizacyjnych obejmujących przedział od 1 do 18 godzin, a które wykazały, że po około 3 godzinach dalsze wydłużanie czasu ekspozycji nie wpływało znacząco na rejestrowane sygnały elektrochemiczne. Po tym czasie na powierzchnię roboczą elektrody sitodrukowanej nanosiłem 50 μL zoptymalizowanego roztworu zawierającego 1% PAA w $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ oraz jony Cu^{2+} o stężeniu $2 \times 10^{-4} \text{ mol L}^{-1}$ (stężenia ustalone na podstawie wcześniejszych badań), pokrywając nim powierzchnię wszystkich trzech elektrod, po czym elektrodę umieszczałem wewnątrz komory. Wspomniana wcześniej zdolność PAA do absorpcji gazu pozwoliła na zapewnienie równowagi na granicy faz ciecz/gaz już po 3 minutach. Analogicznie, czas ten został ustalony na podstawie wcześniejszych badań optymalizacyjnych, z których wynikało, że najwyższe wartości prądowe uzyskiwane były właśnie po 3 minutach ekspozycji elektrolitu na gazowy H_2O_2 . Zarówno skrócenie, jak i wydłużenie tego czasu skutkowało zmniejszeniem odpowiedzi układu. Po tym czasie ekspozycji na atmosferę wypełnioną gazowym nadtlakiem wodoru wykonywałem pomiar elektrochemiczny techniką SWV, próbując sygnał przy potencjale -0.75 V względem srebrnej elektrody quasi-odniesienia, co odpowiadało -0.45 V dla konwencjonalnej elektrody Ag/AgCl . Przeprowadzone trzy serie pomiarowe wykazały liniową zależność rejestrowanego natężenia prądu od stężenia gazowego H_2O_2 w dwóch zakresach stężeń: od 3.7×10^{-11} do $3.7 \times 10^{-10} \text{ mol L}^{-1}$ oraz od 3.7×10^{-10} do $2.6 \times 10^{-9} \text{ mol L}^{-1}$. Stężenia gazowego nadtlenu wodoru zostały oszacowane zgodnie z prawem Henry'ego [69, 70]. Otrzymane zależności kalibracyjne charakteryzowały się bardzo dobrą liniowością, natomiast wartości odchylenia standardowego potwierdzały wysoką powtarzalność opracowanej metody.

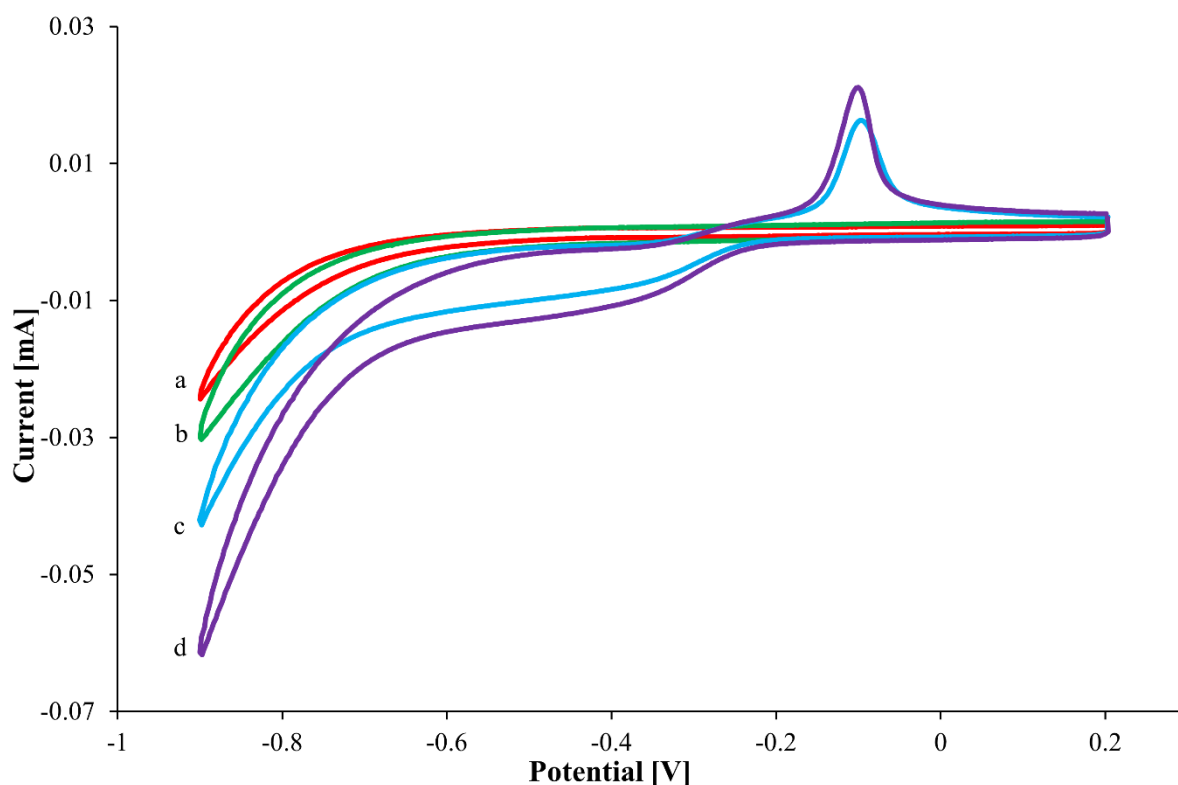
Połączenie właściwości sorpcyjnych PAA z elektrokatalitycznym działaniem jonów miedzi(II) umożliwiło skuteczne oznaczanie nadtlenu wodoru bezpośrednio z fazy gazowej przy zachowaniu wysokiej czułości oraz dobrej powtarzalności pomiarów. Opracowany sposób detekcji pozwalał na oznaczanie śladowych ilości gazowego H_2O_2 , osiągając granicę wykrywalności na poziomie $5.6 \times 10^{-12} \text{ mol L}^{-1}$.



Schemat 1. Proponowany przebieg reakcji dla elektrokatalitycznego mechanizmu drugiego rodzaju odpowiedzialnego za powstawanie ogona katodowego (z ang. *cathodic tail*) przy potencjałach bardziej ujemnych niż -0.400 V . Za zgodą z artykułu [63].

Po opracowaniu układu umożliwiającego elektrochemiczną detekcję gazowego nadtlenu wodoru skupiłem się na poprawie parametrów analitycznych sensora poprzez zastosowanie komercyjnie dostępnych elektrod sitodrukowanych modyfikowanych błękitem pruskim (PB) oraz ftalocyjaniną kobaltu(II) (CoPC). Założyłem, że obecność dodatkowych mediatorów redoks na powierzchni elektrody może wpływać korzystnie na przebieg procesów elektrokatalitycznych, prowadząc do zwiększenia czułości detekcji H_2O_2 . Zarówno błękit pruski, jak i ftalocyjanina kobaltu należą do dobrze poznanych i szeroko opisywanych w literaturze elektrokatalizatorów dla nadtlenu wodoru wykazujących zdolność do efektywnego pośredniczenia w transferze elektronów pomiędzy elektrodą a analitem. W prowadzonych badaniach niezmodyfikowana elektroda sitodrukowana stanowiła punkt odniesienia dla oceny wpływu zastosowanych modyfikatorów na właściwości elektrochemiczne sensora.

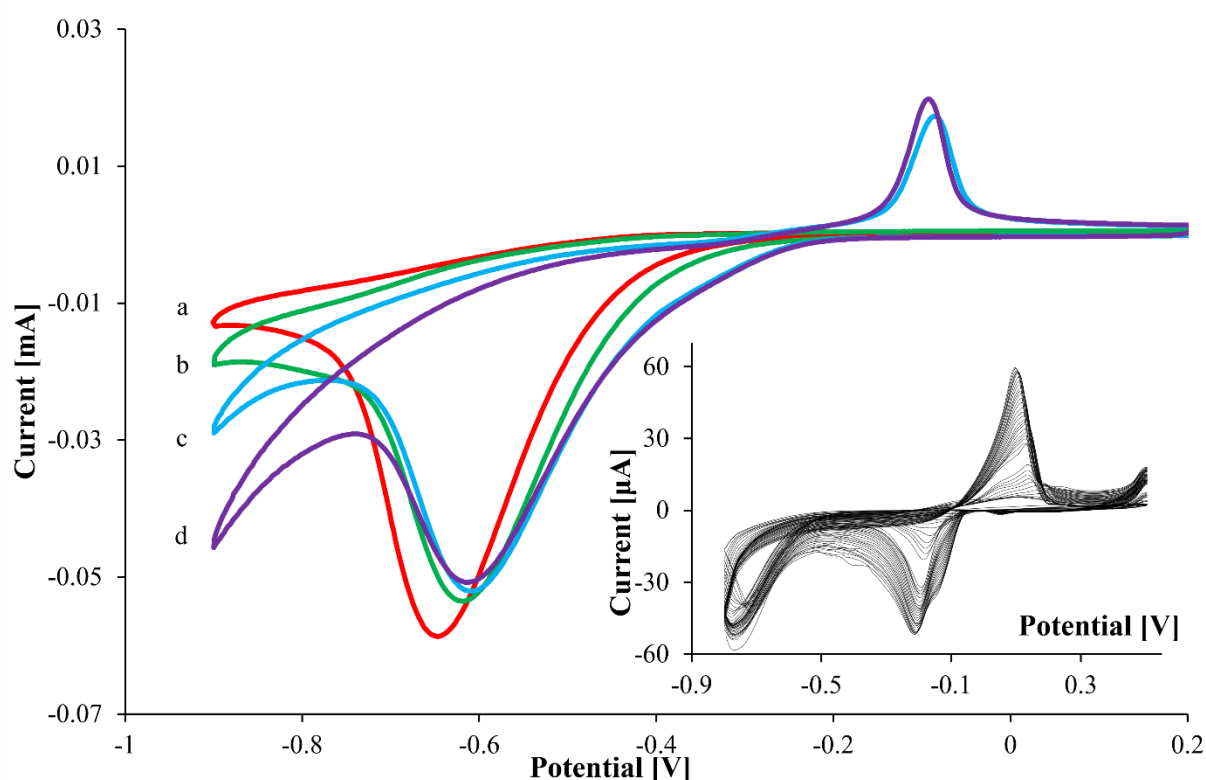
Dlatego też ponownie przeanalizowałem wpływ jonów Cu^{2+} oraz nadtlenu wodoru na przebieg procesów elektrochemicznych zachodzących na niezmodyfikowanych elektrodach sitodrukowanych (Rys. 2). Obecność jonów miedzi(II) prowadziła do wyraźnego wzrostu prądów katodowych związanych zarówno z redukcją tlenu, jak i nadtlenu wodoru, co potwierdzało elektrokatalityczny charakter badanego procesu. Jednoczesna obecność H_2O_2 i Cu^{2+} powodowała dodatkowe zwiększenie odpowiedzi prądowej oraz przesunięcie sygnałów w kierunku potencjałów mniej ujemnych, co było zgodne z wcześniej proponowanym mechanizmem regeneracyjnym typu EC'.



Rysunek 2. Cykliczne woltamperogramy zarejestrowane na niezmodyfikowanej elektrodzie sitodrukowanej w elektrolicie podstawowym składającym się z 0.1 mol L^{-1} KNO_3 oraz 1% PAA. (a) Czysty elektrolit, (b) elektrolit z dodatkiem 1 mmol L^{-1} nadtlenu wodoru, (c) elektrolit z dodatkiem $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów miedzi(II), (d) elektrolit w obecności zarówno Cu^{2+} , jak i H_2O_2 . Szybkość skanowania 50 mV s^{-1} . Za zgodą z artykułu [71].

Odmienny charakter odpowiedzi elektrochemicznej obserwowałem dla elektrod modyfikowanych ftalocyjaniną kobaltu(II) (Rys. 3). W porównaniu do niezmodyfikowanej SPE widoczne było wyraźne zwiększenie sygnałów katodowych, szczególnie w zakresie potencjałów około -0.6 V , co było związane z elektrokatalitycznymi właściwościami warstwy CoPC wobec nieodwracalnej redukcji tlenu. Obecność nadtlenu wodoru powodowała przesunięcie sygnałów w kierunku potencjałów mniej ujemnych oraz dalsze zwiększenie odpowiedzi prądowej, wskazując na wzajemne oddziaływanie procesów redukcji tlenu i H_2O_2 zachodzących poprzez złożone mechanizmy elektrodowe zależne od adsorpcji. Dodatkowo rejestracja kolejnych cykli woltamperometrycznych prowadziła do zmian charakteru odpowiedzi elektrochemicznej, wskazujących na zachodzenie procesów redoks bezpośrednio w warstwie modyfikatora (dodatkowy rysunek, Rys. 3).

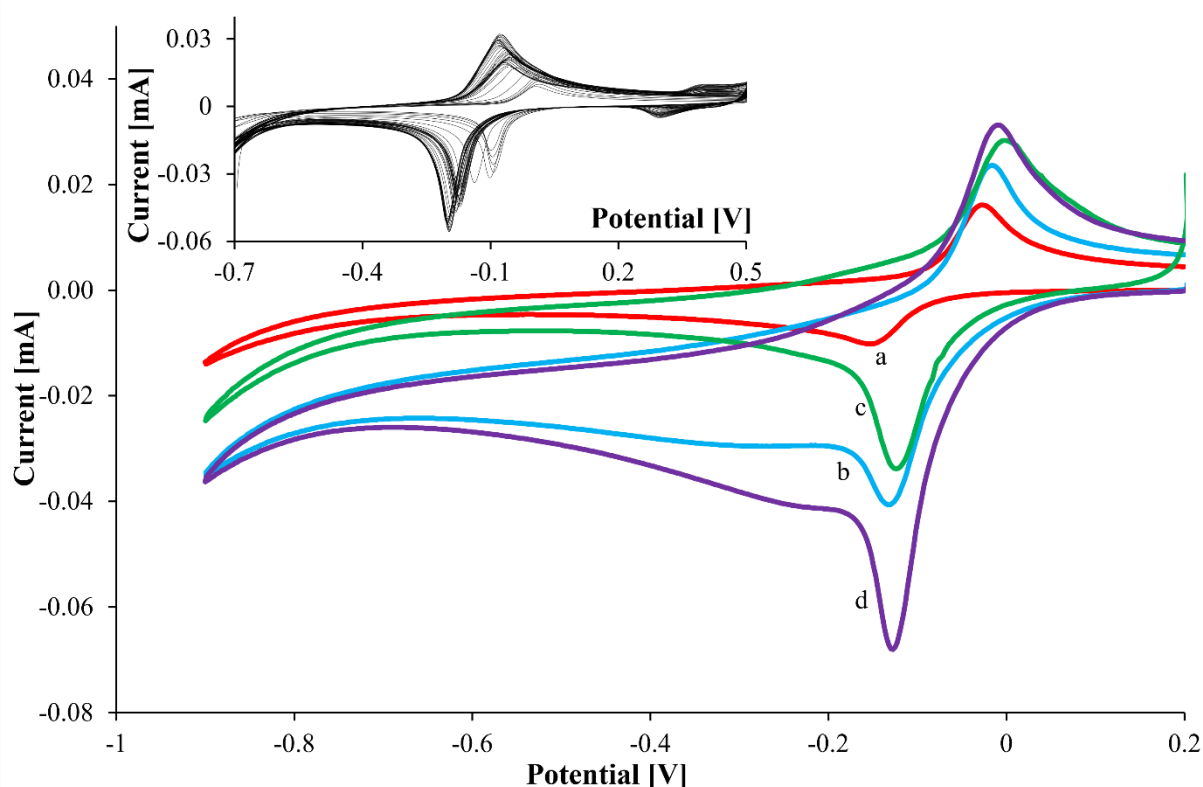
Złożony charakter uzyskiwanych sygnałów utrudniał jednak jednoznaczną interpretację odpowiedzi elektrochemicznej oraz ograniczał selektywność opracowanego układu.



Rysunek 3. Cykliczne woltamperogramy zarejestrowane na elektrodzie sitodrukowanej modyfikowanej ftalocyjaniną kobaltu(II) w elektrolicie podstawowym składającym się z $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ oraz 1% PAA. (a) Czysty elektrolit, (b) elektrolit z dodatkiem 1 mmol L^{-1} nadtlenu wodoru, (c) elektrolit z dodatkiem $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów miedzi(II), (d) elektrolit w obecności zarówno Cu^{2+} , jak i H_2O_2 . Szybkość skanowania 50 mV s^{-1} . Dodatkowy rysunek: kolejne cykle woltamperometryczne zarejestrowane dla elektrody CoPC-SPE w szerokim zakresie potencjałów przy szybkości skanowania 50 mV s^{-1} . Za zgodą z artykułu [71].

Najkorzystniejsze właściwości elektrochemiczne uzyskałem dla elektrod modyfikowanych błękitem pruskim (PB-SPE) (Rys. 4). Woltamperogramy rejestrowane dla tego układu charakteryzowały się obecnością wyraźnych sygnałów redoks związanych z przemianami błękitu pruskiego i bieli pruskiej (PW). Rejestracja kolejnych cykli w szerokim zakresie potencjałów potwierdzała dobrą stabilność odpowiedzi elektrochemicznej oraz odwracalny charakter przemian zachodzących w warstwie modyfikatora (dodatkowy rysunek, Rys. 4). Obecność nadtlenu wodoru prowadziła do wyraźnego zwiększenia sygnałów katodowych związanych z układem PB/PW,

potwierdzając silne właściwości elektrokatalityczne błękitu pruskiego wobec redukcji H_2O_2 . Wzrost odpowiedzi elektrochemicznej obserwowałem również po wprowadzeniu samych jonów Cu^{2+} do systemu, co sugerowało złożoną interakcję pomiędzy modyfikatorem a katalizatorem. Jednakże, to przy jednoczesnej obecności jonów miedzi(II) oraz nadtlenu wodoru widoczny był największy wzrost mierzonych prądów w układzie z PB. Skala wzrostu rejestrowanego sygnału była znacznie większa niż w przypadku zastosowania samego błękitu pruskiego lub wyłącznie jonów Cu^{2+} , co jednoznacznie wskazywało na synergistyczne współdziałanie obu składników. Wyniki te sugerowały, że PB oraz jony Cu^{2+} uczestniczą w komplementarnych procesach elektrokatalitycznych prowadzących do skutecznej amplifikacji odpowiedzi elektrochemicznej związanej z redukcją H_2O_2 . W mojej ocenie stanowiło to jeden z najistotniejszych rezultatów tego etapu badań, gdyż wskazywało to na możliwość wykorzystania połączenia pomiędzy klasycznym modyfikatorem powierzchni elektrody z rozpuszczalnym mediatorem redoks do znaczącej poprawy parametrów detekcyjnych układu.



Rysunek 4. Cykliczne woltamperogramy zarejestrowane na elektrodzie sitodrukowanej modyfikowanej błękitem pruskim w elektrolicie podstawowym składającym się z $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ oraz 1% PAA. (a) Czysty elektrolit, (b) elektrolit z dodatkiem 1 mmol L^{-1} nadtlenu wodoru, (c) elektrolit z dodatkiem $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów miedzi(II), (d) elektrolit w obecności zarówno Cu^{2+} , jak i H_2O_2 . Szybkość skanowania 50 mV s^{-1} .

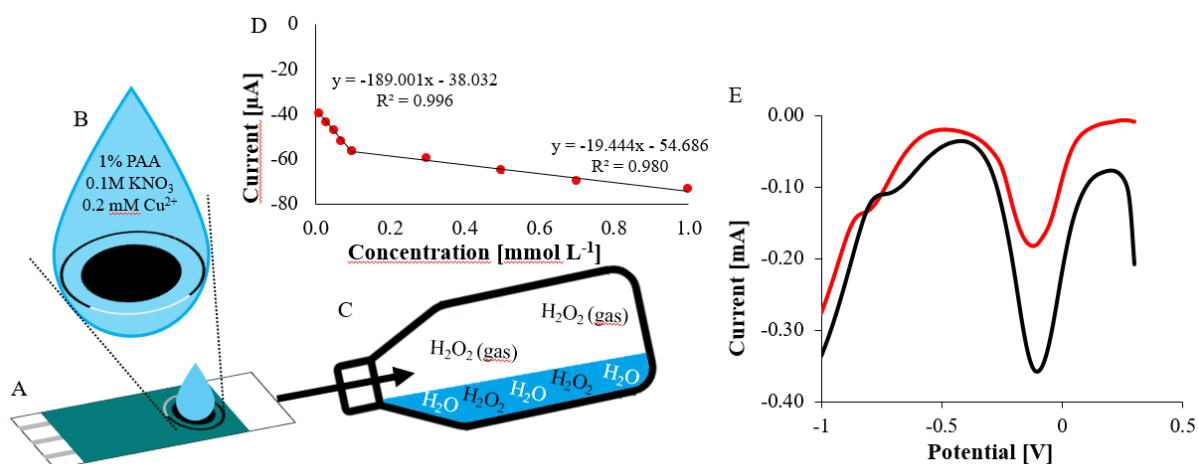
Dodatkowy rysunek: kolejne cykle woltamperometryczne zarejestrowane dla elektrody PB-SPE w tym samym elektrolicie podstawowym przy szybkości skanowania 50 mV s^{-1} . Za zgodą z artykułu [71].

Dalszą charakterystykę zastosowanych elektrod sitodrukowanych przeprowadziłem z wykorzystaniem woltamperometrii fali prostokątnej. Uzyskane przeze mnie wyniki pozostawały zgodne z obserwacjami otrzymanymi metodą CV, potwierdzając korzystny wpływ jonów miedzi(II) oraz zastosowanych modyfikatorów na przebieg procesów elektrokatalitycznych. Zastosowanie techniki SWV pozwoliło mi uzyskać lepszą rozdzielczość sygnałów oraz większą czułość pomiarów, co następnie wykorzystałem do określenia liniowej zależności między prądem na różnych elektrodach a stężeniem nadtlenku wodoru. W celu dokładniejszego porównania właściwości poszczególnych elektrod przeprowadziłem serię pomiarów dla stężeń H_2O_2 z zakresu od 0.1 do 10 mmol L^{-1} w obecności $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów Cu^{2+} . Badania prowadziłem w fazie wodnej. Dla zachowania spójności wyników sygnał prądowy próbkowałem przy potencjale -0.75 V , odpowiadającym obszarowi bezpośredniej redukcji nadtlenku wodoru względem srebrnej elektrody quasi-odniesienia. Wszystkie analizowane elektrody wykazywały liniową zależność odpowiedzi prądowej od stężenia H_2O_2 , jednak uzyskiwane czułości różniły się w zależności od rodzaju zastosowanego modyfikatora. Najwyższe wartości rejestrowanych prądów oraz najlepszą czułość uzyskałem dla niezmodyfikowanej SPE w obecności jonów Cu^{2+} , co wskazywało, że w warunkach bezpośredniej redukcji nadtlenku wodoru układ ten wykazuje najkorzystniejsze właściwości analityczne spośród analizowanych elektrod.

Elektrody modyfikowane błękitem pruskim, mimo że nie wykazywały poprawy parametrów analitycznych w przypadku bezpośredniej redukcji nadtlenku wodoru, pozwoliły mi zaobserwować wyraźną zależność pomiędzy odpowiedzią elektrochemiczną błękitu pruskiego a obecnością H_2O_2 w roztworze zawierającym jony miedzi(II) (Schemat 2E). Obserwacja ta stała się podstawą do opracowania przeze mnie pośredniej metody oznaczania gazowego nadtlenku wodoru, w której zarówno błękit pruski, jak i jony Cu^{2+} synergistycznie przekazywały elektrony między elektrodą a nadtlenkiem wodoru. Stosując analogiczną do opisanej wcześniej procedurę oznaczania gazowego nadtlenku wodoru (Schemat 2A–C) wykorzystałem opracowany układ bazujący na synergistycznym działaniu błękitu pruskiego i jonów miedzi(II). Obecność PAA w elektrolicie podstawowym umożliwiała efektywną absorpcję oraz ponowne rozpuszczanie nadtlenku wodoru z fazy

gazowej, natomiast współdziałanie błękitu pruskiego i jonów Cu^{2+} prowadziło do wyraźnego zwiększenia odpowiedzi elektrochemicznej. Opracowany układ wykazywał liniową odpowiedź w zakresie stężeń gazowego H_2O_2 od $3.7 \times 10^{-12} \text{ mol L}^{-1}$ do $1.85 \times 10^{-9} \text{ mol L}^{-1}$. Zastosowanie błękitu pruskiego jako dodatkowego współkatalizatora umożliwiło obniżenie granicy wykrywalności o około jeden rząd wielkości względem wcześniej opracowanego układu opartego wyłącznie na PAA i jonach miedzi(II), przy jednoczesnej poprawie liniowości oraz powtarzalności pomiarów.

Wykonane przeze mnie badania pokazały, że znane właściwości elektrokatalityczne błękitu pruskiego wobec nadtlenu wodoru mogą zostać dodatkowo wzmocnione poprzez zastosowanie zaproponowanego w niniejszej dysertacji układu pomiarowego opartego na PAA oraz jonach miedzi(II), co pozwoliło na dalszą poprawę parametrów detekcyjnych sensora. Jednocześnie wyniki te zamykały etap badań poświęcony porównaniu wpływu różnych modyfikatorów powierzchni elektrod sitodrukowanych na właściwości analityczne opracowywanych układów pomiarowych.



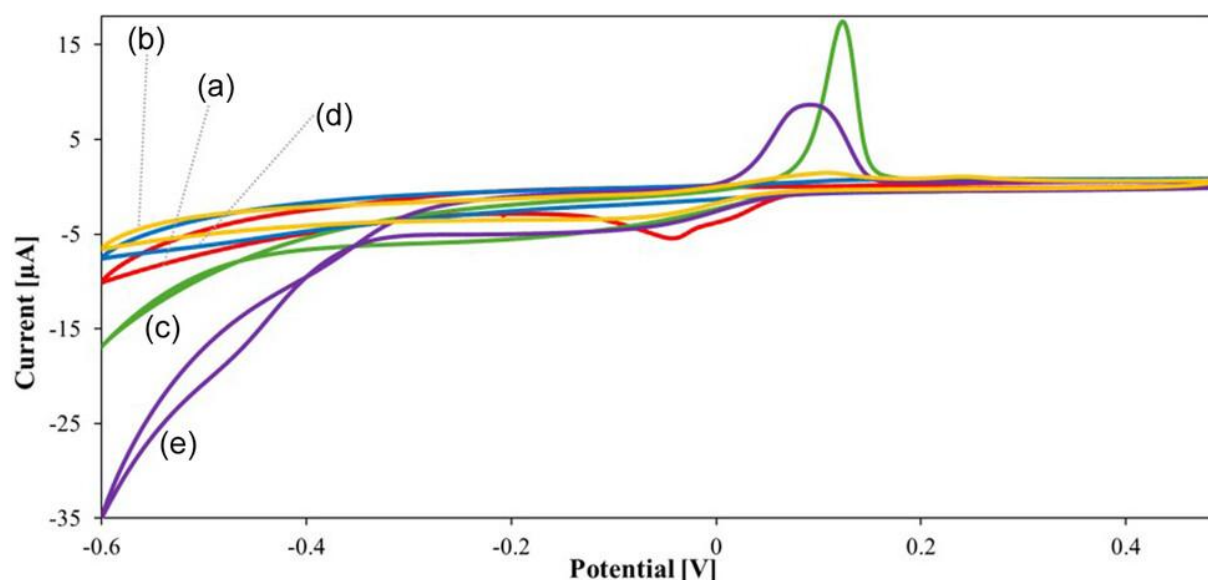
Schemat 2. Schemat układu pomiarowego do detekcji nadtlenu wodoru w fazie gazowej. (A) Elektroda sitodrukowana zawierająca trzy elektrody: węglową elektrodę roboczą, srebrną elektrodę quasi-odniesienia oraz węglową elektrodę pomocniczą, na powierzchnię których naniesiono 50 μL elektrolitu podstawowego zawierającego 1% PAA w 0.1 M KNO_3 oraz $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów miedzi(II). (B) Powiększony widok obszaru roboczego systemu (naniesiony roztwór pokrywa powierzchnię wszystkich trzech elektrod). (C) Szczelnie zamknięta szklana komora zawierająca 50 mL wodnego roztworu nadtlenu wodoru o określonym stężeniu. Po 3 godzinach stabilizacji elektroda z naniesionym roztworem była umieszczana wewnątrz komory. (D) Odpowiedź prądowa w funkcji stężenia nadtlenu wodoru rozpuszczonego w elektrolicie podstawowym ($1 \times 10^{-5} - 1 \times$

$10^{-3} \text{ mol L}^{-1}$) zarejestrowana na elektrodzie sitodrukowanej modyfikowanej błękitem pruskim. (E) Przykładowa odpowiedź SWV zarejestrowana w komorze: ślepa próba (czerwona krzywa) oraz odpowiedź dla 1 mmol L^{-1} nadtlenu wodoru (czarna krzywa). Parametry techniki SWV: amplituda 0.05 V , częstotliwość 8 Hz oraz krok potencjału -0.005 V . Za zgodą z artykułu [71].

Zgodnie z założonymi celami badawczymi, kolejny etap prowadzonych przeze mnie badań obejmował optymalizację składu elektrolitu podstawowego. Dotychczas prowadzone badania wykazały, że kwas poliakrylowy stanowił bardzo korzystne medium dla procesów elektrokatalitycznych zachodzących w obecności jonów miedzi(II), głównie dzięki wysokiej zdolności absorpcji wody, dobrym właściwościom polielektrolitycznym oraz możliwości tworzenia stabilnych cienkich warstw na powierzchni elektrody. Niemniej jednak, w trakcie prowadzonych badań zauważyłem, że dla bardzo niskich stężeń nadtlenu wodoru różnice pomiędzy odpowiedzią elektrochemiczną analitu a sygnałem rejestrowanym dla ślepej próby stają się coraz mniej wyraźne, co ograniczało możliwości dalszego zwiększania czułości tego układu. Dlatego też podjąłem próbę znalezienia nowych materiałów, które mogłyby poprawić czułość oraz stabilność sygnału elektrochemicznego. Na podstawie danych literaturowych wybrałem dwa główne polielektrolity przeznaczone do dalszych badań: kwas poli(2-akrylamido-2-metylo-1-propanosulfonowy) (pAMPS) oraz kopolimer poli(akrylamidu-co-kwasu akrylowego) (pAAmAA). Dodatkowo przeanalizowałem również dwa inne kopolimery, poli(etylen-co-kwas akrylowy) oraz poli(tert-butyloakrylan-co-etyloakrylan-co-kwas metakrylowy), jednak już na początkowym etapie badań wykazywały one niezadowalające właściwości zarówno fizyczne, jak i elektrochemiczne, w związku z czym nie uwzględniłem ich w dalszej części pracy.

Wykonałem analizę elektrochemiczną poszczególnych polielektrolitów z wykorzystaniem voltamperometrii cyklicznej oraz fali prostokątnej, gdzie jako układy odniesienia zastosowałem roztwory KNO_3 oraz PAA. Porównaniu poddałem pAAmAA i dwa warianty pAMPS: formę natywną oraz roztwór zneutralizowany o pH 7. Zastosowanie kopolimeru pAAmAA prowadziło do wyraźnego zwiększenia prądów katodowych odpowiadających bezpośredniej redukcji H_2O_2 w zakresie potencjałów bardziej ujemnych niż -0.4 V (Rys. 5, krzywa b). W porównaniu do wcześniej stosowanego PAA (Rys. 5, krzywa c) układ oparty na kopolimerze wykazywał korzystniejszą odpowiedź

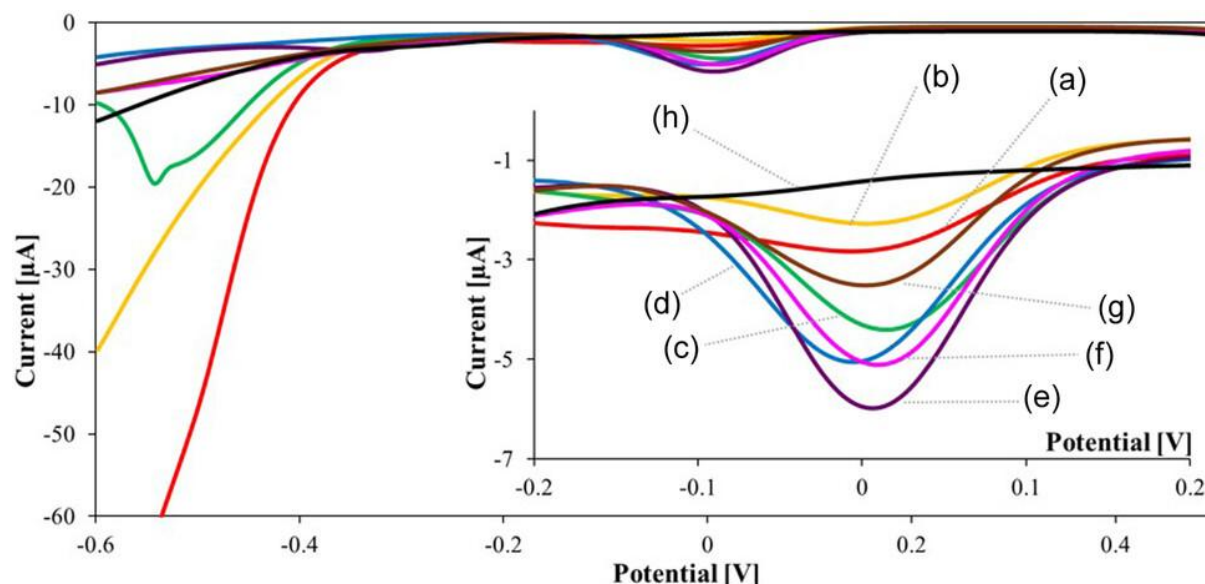
elektrochemiczną, co sugerowało bardziej efektywny przebieg procesów elektrokatalitycznych związanych z redukcją nadtlenu wodoru. Analogiczne zależności potwierdziłem również z wykorzystaniem woltamperometrii fali prostokątnej. Ponadto, przeanalizowałem wpływ stężenia pAAmAA na charakter odpowiedzi elektrochemicznej. Najlepsze właściwości systemu uzyskałem dla roztworu zawierającego 1% kopolimeru, natomiast dalsze zwiększanie jego stężenia prowadziło do stopniowego obniżania intensywności sygnałów elektrochemicznych. Zjawisko to powiązałem ze wzrostem lepkości roztworu oraz ograniczeniem możliwości dyfuzji elektroaktywnych form w elektrolicie podstawowym. Co więcej, pomimo że pAAmAA wykazywał obiecujące właściwości w pomiarach fazy gazowej, poprawa granicy detekcji względem wcześniejszego systemu opartego na PAA była mocno ograniczona.



Rysunek 5. Cykliczne woltamperogramy zarejestrowane na GCE w wybranych elektrolitach podstawowych: (a) $0.1 \text{ mol L}^{-1} \text{ KNO}_3$, (b) pAAmAA, (c) PAA, (d) pAMPS oraz (e) zneutralizowany pAMPS (pH 7). Każdy z badanych polielektrolitów stosowano w stężeniu 1% (w/v). Wszystkie analizowane roztwory przygotowano w $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ z dodatkiem 1 mmol L^{-1} nadtlenu wodoru oraz $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów miedzi(II). Szybkość skanowania 50 mV s^{-1} . Za zgodą z artykułu [72].

Najlepsze rezultaty uzyskałem dla pAMPS w roli elektrolitu podstawowego. Początkowo jego natywna forma (Rys. 5, krzywa d) charakteryzowała się bardzo silnymi właściwościami kompleksującymi jony Cu^{2+} (wynikającymi z obecności grup sulfonowych), co w konsekwencji prowadziło do zmniejszenia ich elektrochemicznej dostępności i tym samym do osłabienia efektu elektrokatalitycznego. Analiza

woltamperogramów pokazała wyraźne osłabienie sygnału redukcji jonów miedzi w pobliżu 0 V oraz stosunkowo niewielkie prądy katodowe związane z bezpośrednią redukcją nadtlenu wodoru. Neutralizacja pAMPS prowadziła natomiast do zwiększenia elektrochemicznej dostępności jonów Cu^{2+} oraz wyraźnego wzrostu prądów katodowych przy potencjałach bardziej ujemnych (Rys. 5, krzywa e). Obserwowane zmiany odpowiedzi elektrochemicznej po zobojętnieniu pAMPS skłoniły mnie do przeprowadzenia szczegółowej analizy wpływu pH na właściwości polielektrolitu. Otrzymane wyniki wykazały, że roztwór pAMPS o pH 2 najkorzystniej wspierał bezpośrednią redukcję nadtlenu wodoru, przy jednoczesnym ograniczeniu właściwości kompleksujących względem jonów Cu^{2+} (Rys. 6). W efekcie pozwoliło to na wyraźny wzrost odpowiedzi prądowej przy potencjałach mocno ujemnych związanych z redukcją nadtlenu wodoru.



Rysunek 6. Woltamperogramy fali prostokątnej zarejestrowane na GCE w 1% roztworach pAMPS o różnych wartościach pH: (a) 2, (b) 2.5, (c) 3.5, (d) 4, (e) 4.44, (f) 6, (g) 7 oraz (h) 9.8. Wszystkie analizowane roztwory zawierały 1 mmol L^{-1} nadtlenu wodoru oraz $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów miedzi(II). Dodatkowy rysunek: powiększony fragment przedstawiający reakcje redoks jonów miedzi(II). Parametry techniki SWV: amplituda 0.050 V, częstotliwość 8 Hz, krok potencjału -0.005 V . Za zgodą z artykułu [72].

Detekcję gazowego nadtlenu wodoru z wykorzystaniem pAMPS prowadziłem przy użyciu elektrod sitodrukowanych, stosując analogiczną procedurę pomiarową do opisanej wcześniej. Początkowo pomiary wykonywane na niezmodyfikowanych SPE nie zapewniały jednak wystarczającej czułości oraz powtarzalności. W celu poprawy właściwości detekcyjnych zastosowałem elektrody modyfikowane błękitem pruskim,

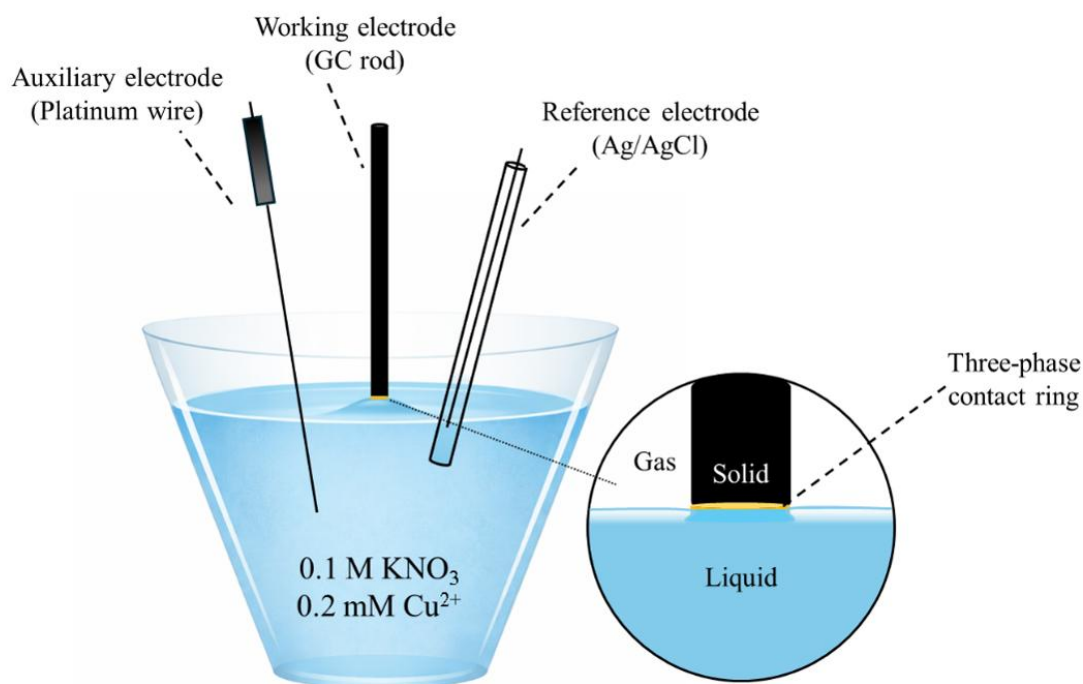
których efekt synergistyczny z jonami miedzi(II) potwierdziłem we wcześniejszych badaniach. Ostatecznie, wybór pAMPS o pH 2 w połączeniu z PB-SPE oraz jonami miedzi(II) umożliwił czułą i powtarzalną detekcję gazowego nadtlenu wodoru. Opracowany układ wykazywał liniową odpowiedź w zakresie stężeń od 3.7×10^{-11} do 3.7×10^{-10} mol L⁻¹ (obliczone na podstawie prawa Henry'ego), natomiast uzyskane wartości odchylenia standardowego potwierdzały wysoką stabilność i powtarzalność pomiarów.

Uzupełnieniem prowadzonych badań była próba opracowania przeze mnie układów mieszanych opartych na różnych polielektrolitach, mająca na celu połączenie najkorzystniejszych właściwości poszczególnych materiałów. Najbardziej obiecująca okazała się mieszanina pAMPS i pAAmAA w stosunku objętościowym 1:1, która umożliwiała skuteczną detekcję gazowego nadtlenu wodoru, jednakże jej czułość nadal pozostawała niższa niż w przypadku zoptymalizowanego pAMPS o pH 2. Pozostałe kombinacje polielektrolitów, czyli układy PAA-pAMPS oraz PAA-pAAmAA, nie wykazywały korzystnych właściwości analitycznych.

Przeprowadzone przeze mnie badania potwierdziły, że zarówno dobór elektrolitu podstawowego, jak i kontrola oddziaływań pomiędzy analitem, elektrokatalizatorem oraz polielektrolitem mają bezpośredni wpływ na przebieg procesów elektrokatalitycznych i parametry opracowywanych sensorów.

Zwieńczeniem mojej pracy badawczej było opracowanie układu pomiarowego wykorzystującego detekcję na granicy trzech faz (TPB) obejmującej fazę gazową, ciekłą oraz stałą. Celem nowego układu było zwiększenie efektywności oznaczania gazowego nadtlenu wodoru poprzez skrócenie czasu analizy przy jednoczesnym obniżeniu granicy wykrywalności. Było to zupełnie nowe podejście do oznaczania H₂O₂, stanowiące alternatywę względem klasycznych układów dwufazowych. W proponowanym rozwiązaniu obecność TPB sprzyja efektywnemu transportowi gazowego analitu do powierzchni elektrody oraz ogranicza wpływ procesów zachodzących w objętości roztworu. Dzięki temu możliwe było prowadzenie bezpośrednich oznaczeń gazowego nadtlenu wodoru przy jednoczesnym uproszczeniu składu elektrolitu podstawowego. Opracowany układ badawczy został przedstawiony na Schemacie 3. Zaproponowana przeze mnie konfiguracja prowadziła do utworzenia w formie pierścienia granicy trzech faz w miejscu kontaktu powierzchni elektrody roboczej z elektrolitem oraz atmosferą nasyconą nadtlakiem wodoru. Rozwiązanie to pozwalało na bezpośredni transport gazowego H₂O₂ do powierzchni elektrody przy jednoczesnym zachowaniu przewodnictwa jonowego

zapewnianego przez obecność ciekłego elektrolitu. W porównaniu do klasycznych dwufazowych układów pomiarowych system ten zapewniał lepsze warunki wymiany ładunku w obszarze granicy faz. Połączenie tych właściwości umożliwiło uzyskanie wysokiej czułości oraz selektywności detekcji gazowego H_2O_2 .

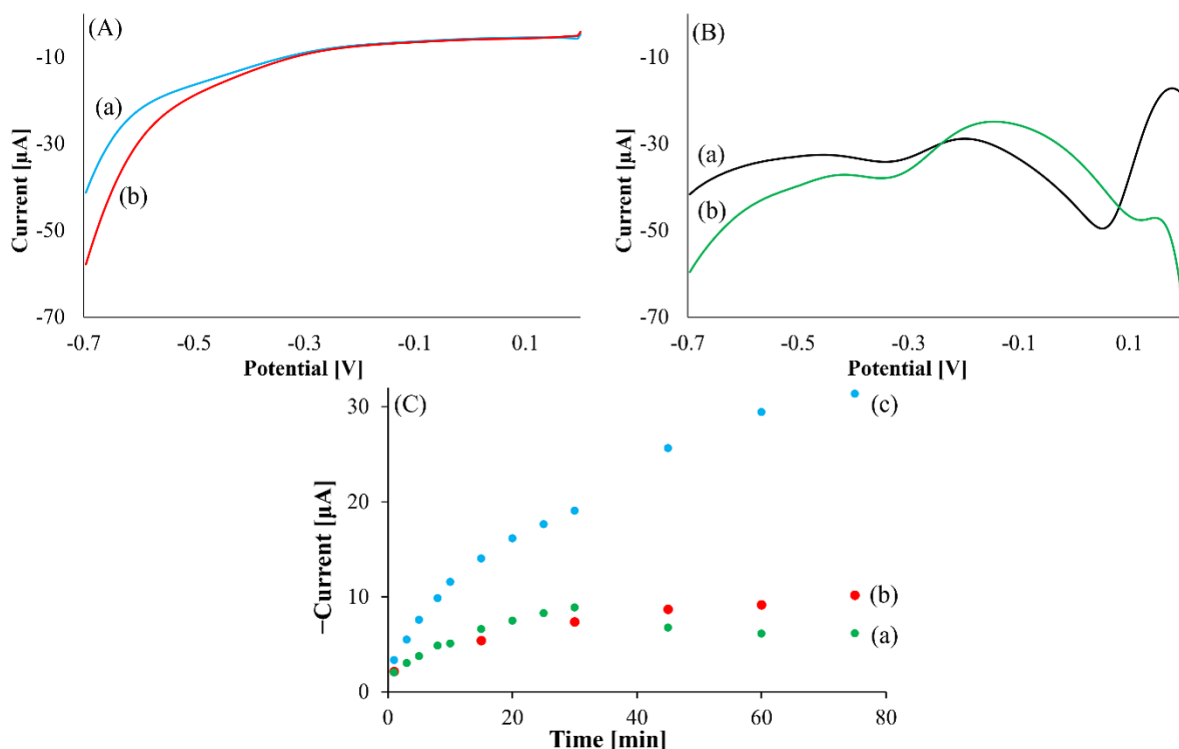


Schemat 3. Schemat zaproponowanego układu pomiarowego wykorzystującego granicę trzech faz. Za zgodą z artykułu [77].

W ramach badań nad nowym układem przeprowadziłem porównanie różnych materiałów elektrodowych mające na celu określenie odpowiedniej elektrody pracującej. Kluczowymi kryteriami wyboru elektrody były możliwość stabilnego formowania granicy trzech faz oraz zdolność do efektywnego wspierania elektrochemicznej redukcji H_2O_2 . Do analizy wybrałem między innymi siatki miedziane i złote, druty platynowe i złote, elektrodę grafitową impregnowaną parafiną oraz prętową elektrodę z węgla szklistego. Część z tych materiałów została przeze mnie odrzucona już na wstępnym etapie badań ze względu na niestabilność sygnału, intensywne wydzielanie wodoru lub problemy z utrzymaniem stabilnej granicy faz. Ostatecznie, do dalszych badań zakwalifikowałem PIGE oraz GCER. Spośród tej dwójki najlepsze właściwości wykazywał pręt z węgla

szklistego, który zapewniał najwyższą stabilność sygnału, największą odpowiedź prądową oraz dobrą powtarzalność pomiarów.

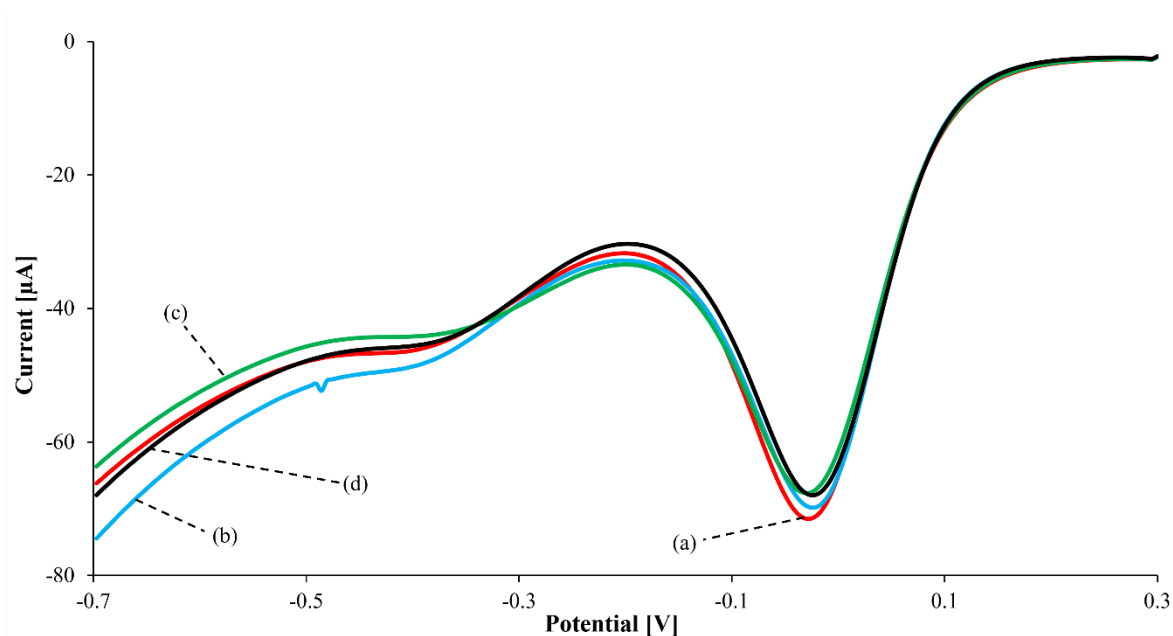
Ważnym elementem badań była optymalizacja składu elektrolitu podstawowego dla nowo opracowanego układu trójfazowego. Co prawda, wcześniejsze badania pozwoliły mi wskazać najbardziej korzystne układy elektrolitowe do detekcji gazowego nadtlenu wodoru, tak zastosowanie całkowicie nowej konfiguracji pomiarowej wymagało ponownej ich weryfikacji. Bazując na wcześniejszych doświadczeniach związanych z wykorzystaniem polielektrolitów w detekcji gazowego nadtlenu wodoru, do porównania wybrałem roztwór $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ oraz układy zawierające dodatkowo PAA oraz pAMPS o pH 2. W każdym z nich jony Cu^{2+} pełniły funkcję elektrokatalizatora. Równocześnie, przeprowadziłem badania określające czas niezbędny do wysycenia komory pomiarowej (całkowita objętość komory wynosiła 150 mL) gazowym H_2O_2 w każdym elektrolicie. W tym celu monitorowałem zmiany odpowiedzi elektrochemicznej podczas nasycania komory parami H_2O_2 generowanymi z wodnego roztworu nadtlenu wodoru przez okres 75 minut. Reprezentatywne woltamperogramy SW zarejestrowane po 30 minutach zostały przedstawione na Rys. 7A i B. Wyniki pokazały, że obecność polielektrolitów znacząco zwiększała rozpuszczalność H_2O_2 w fazie ciekłej, co całkowicie uniemożliwiało nasycenie komory jego parami (Rys. 7C). Szczególnie widoczne było to dla układu zawierającego PAA, gdzie wysoka zdolność absorpcji nadtlenu wodoru wpływała na charakter rejestrowanej odpowiedzi elektrochemicznej oraz wydłużała całkowity czas stabilizacji układu. Odmienne rezultaty otrzymałem dla samego roztworu KNO_3 zawierającego jony Cu^{2+} , dla którego wysycenie atmosfery parami H_2O_2 obserwowałem już po 30 minutach. Wyniki te wskazywały, że w przypadku układu trójfazowego uproszczenie składu elektrolitu podstawowego pozwalało uzyskać korzystniejsze warunki detekcji niż wcześniej stosowane układy polielektrolitowe.



Rysunek 7. Woltamperogramy fali prostokątnej zarejestrowane w układzie trójfazowym dla różnych elektrolitów podstawowych zawierających 2×10^{-4} mol L⁻¹ jonów Cu²⁺: (A) 1% PAA w 0.1 M KNO₃ oraz (B) wyłącznie 0.1 M KNO₃; krzywe: (a) ślepa próba oraz (b) po ekspozycji na gazowy H₂O₂. (C) Względna odpowiedź prądowa w funkcji czasu nasycenia po wprowadzeniu 1 mM H₂O₂ do 5 mL wody znajdującej się w oddzielnym naczyniu wewnątrz szczelnie zamkniętej komory o objętości 150 mL, dla różnych elektrolitów podstawowych: (a) 0.1 M KNO₃, (b) 1% PAA oraz (c) 1% pAMPS (zarówno (b), jak i (c) w 0.1 M KNO₃). Parametry SWV: częstotliwość 8 Hz, amplituda 0.050 V, potencjał kroku -0.005 V. Za zgodą z artykułu [77].

W celu potwierdzenia rzeczywistego udziału TPB w procesie detekcji przeprowadziłem dodatkowe eksperymenty kontrolne. Porównałem odpowiedź elektrochemiczną uzyskiwaną dla elektrody swobodnie tworzącej granicę styku trzech faz z odpowiedzią tej samej elektrody, ale częściowo zabezpieczonej warstwą izolującą uniemożliwiającą formowanie TPB. Technika SWV zarejestrowałem woltamperogramy zarówno dla ślepej próby (Rys. 8, krzywa a), jak i po wysyceniu komory parami nadtlenu wodoru (Rys. 8, krzywa b). Analogiczne pomiary przeprowadziłem dla elektrody zabezpieczonej warstwą izolującą (Rys. 8, krzywe c i d). Ograniczenie formowania TPB praktycznie nie wpływało na sygnał związany z redukcją jonów miedzi(II) w zakresie potencjałów około 0.05 V. Wskazuje to na to, że konwencjonalna reakcja elektrodowa

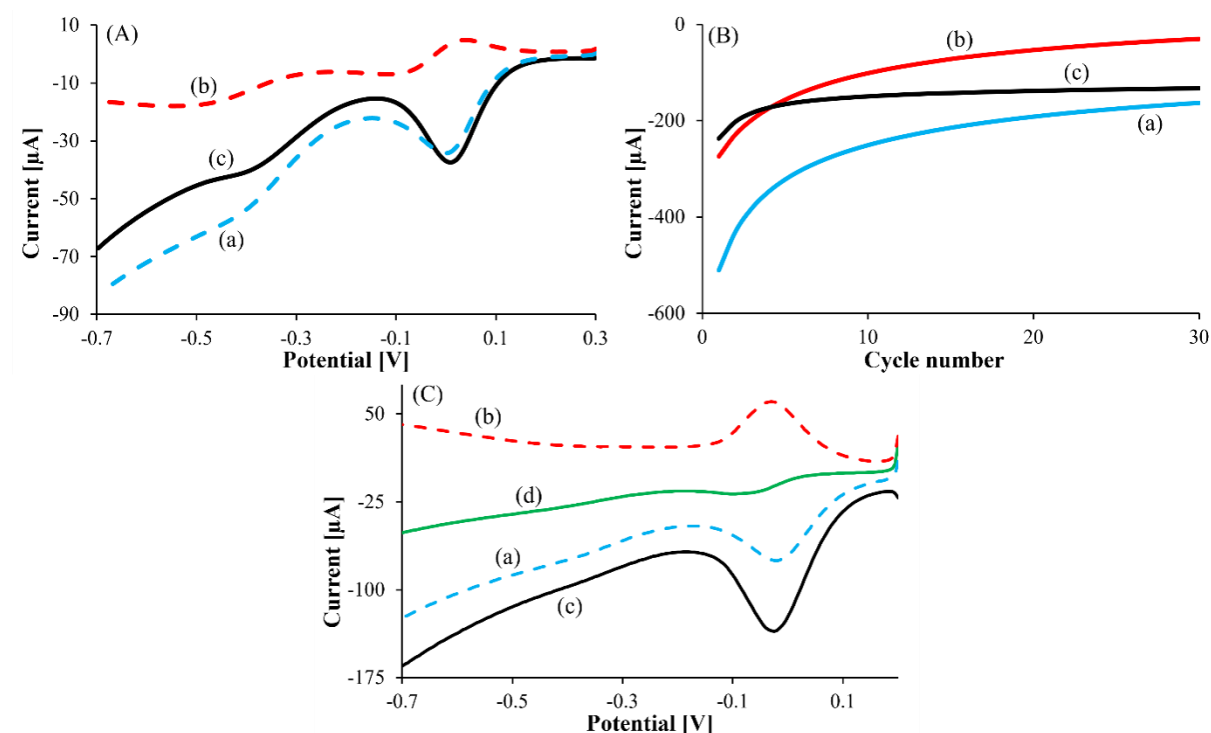
redukcji Cu^{2+} zachodziła na pozostałej części powierzchni elektrody mającej kontakt wyłącznie z fazą wodną. Jednocześnie ślepe próby zarejestrowane dla elektrody z zabezpieczoną TPB oraz wyeksponowaną pozostawały niemal identyczne. Wyraźne różnice pomiędzy obiema elektrodami pojawiały się natomiast w zakresie ogona katodowego już po wypełnieniu komory parami H_2O_2 , na korzyść elektrody tworzącej TPB. Wyniki te potwierdziły więc to, że wzrost odpowiedzi prądowej był bezpośrednio związany z procesami zachodzącymi w obrębie granicy trzech faz i stanowił efekt działania opracowanego układu trójfazowego.



Rysunek 8. Woltamperogramy fali prostokątnej zarejestrowane dla dwóch wariantów GCER w elektrolicie podstawowym składającym się z $0.1 \text{ mol L}^{-1} \text{KNO}_3$ i $2 \times 10^{-4} \text{ mol L}^{-1}$ jonów Cu^{2+} : z ekspozycją granicy trójfazowej, gdzie (a) ślepa próba, (b) po kontakcie z gazowym H_2O_2 ; z zablokowaną granicą trójfazową, gdzie (c) ślepa próba, (d) po ekspozycji na gazowy H_2O_2 . Stężenie nadtlenu wodoru 1 mmol L^{-1} . Parametry SWV: częstotliwość 8 Hz, amplituda 0.050 V, potencjał kroku -0.005 V .

Ocenę możliwości analitycznych opracowanego układu trójfazowego przeprowadziłem z wykorzystaniem nie tylko klasycznej woltamperometrii fali prostokątnej, ale również niedawno opracowanych zaawansowanych technik, w tym elektrochemicznej spektroskopii faradajowskiej i różnicowej woltamperometrii fali prostokątnej, co stanowiło końcowy etap badań prowadzonych w ramach niniejszej rozprawy. Reprezentatywne odpowiedzi elektrochemiczne uzyskane z wykorzystaniem wszystkich trzech technik przedstawiłem na Rys. 9. Pomiary wykonane klasyczną SWV

potwierdziły możliwość prowadzenia stabilnych i wysoce powtarzalnych oznaczeń gazowego H_2O_2 w bardzo szerokim zakresie stężeń, tj. od 1.85×10^{-12} do 2.96×10^{-11} mol L^{-1} (obliczone na podstawie prawa Henry’ego). Wyznaczona granica wykrywalności wynosiła 1.28×10^{-13} mol L^{-1} . Uzyskana zależność charakteryzowała się bardzo dobrą liniowością ($R^2 = 0.999$), a średnia wartość względnego odchylenia standardowego dla trzech niezależnych serii pomiarowych była równa 3.3%, co potwierdzało wysoką powtarzalność układu.



Rysunek 9. Porównanie odpowiedzi elektrochemicznych uzyskanych z wykorzystaniem różnych technik woltamperometrycznych w trójfazowym układzie gaz–ciecz–ciało stałe: (A) SWV, (B) elektrochemiczna spektroskopia faradajowska oraz (C) różnicowa woltamperometria fali prostokątnej. Pomiary wykonano w elektrolicie podstawowym 0.1 M KNO_3 zawierającym 2×10^{-4} mol L^{-1} jonów Cu^{2+} w obecności gazowego H_2O_2 ; (a) składowa forward, (b) składowa backward, (c) odpowiedź wynikowa oraz (d) składowa step. Za zgodą z artykułu [77].

Dalszą poprawę parametrów analitycznych udało mi się uzyskać stosując technikę EFS, ze względu na skuteczniejsze rozdzielenie prądów faradajowskich od pojemnościowych, na które pozwala ta technika. W przeciwieństwie do SWV, odpowiedź elektrochemiczną analizowałem w postaci funkcji kolejnych cykli zmian potencjału, a końcowy sygnał analityczny wyznaczałem poprzez uśrednienie prądów netto

z ostatnich pięciu cykli po odjęciu ślepej próby. Taka metodologia pozwoliła mi na obniżenie granicy wykrywalności aż do $7.79 \times 10^{-14} \text{ mol L}^{-1}$, z jednoczesnym zachowaniem liniowej odpowiedzi w zakresie od 3.7×10^{-13} do $3.7 \times 10^{-12} \text{ mol L}^{-1}$. Pomimo bardziej złożonego układu system zachowywał dobrą powtarzalność, osiągając średnie RSD na poziomie 5.3%.

Niemniej jednak, najkorzystniejsze właściwości analityczne uzyskałem stosując DSWV. W technice tej każdy cykl potencjału składał się z kroku potencjału, po którym następowały dwa impulsy o przeciwnej polaryzacji. W rezultacie otrzymałem liniową zależność analityczną w zakresie od 3.7×10^{-14} do $3.7 \times 10^{-13} \text{ mol L}^{-1}$, a granicę wykrywalności udało mi się obniżyć do poziomu $2.79 \times 10^{-15} \text{ mol L}^{-1}$. Jednocześnie pomiary DSWV charakteryzowały się bardzo wysoką precyzją pomiarów, osiągając średnie względne odchylenie standardowe na poziomie jedynie 1.3%. W konsekwencji metoda ta, wedle mojej najlepszej wiedzy (Tabela 1.), należy do najczulszych spośród dostępnych dotychczas metod elektrochemicznego oznaczania gazowego nadtlenu wodoru i potwierdzając tym samym, że połączenie układu trójfazowego z zaawansowanymi technikami impulsowymi stanowi bardzo skuteczne narzędzie ultraczułej detekcji śladowych ilości H_2O_2 w fazie gazowej.

Tabela 1. Porównanie zaproponowanych w niniejszej dysertacji metod detekcji nadtlenu wodoru z danymi literaturowymi.

Rodzaj sensora	Metoda	Faza	Zakres liniowy (mol L^{-1})	LOD (mol L^{-1})	Ref.
Skruber dyfuzyjny	CL	Gazowa	2.45×10^{-11} – 1.39×10^{-10}	---	[48]
Skruber dyfuzyjny	CL	Gazowa	---	1.0×10^{-12}	[49]
Pt-SPE/ Nafion®	Amperometria	Gazowa	---	1.6×10^{-9}	[73]
Skruber dyfuzyjny	Kolorymetria	Gazowa	---	1.1×10^{-12}	[51]
Czujnik hydrożelowy HRP/BSA (2-D PhC)	Kolorymetria	Wodna	8.8×10^{-6} – 6.06×10^{-5}	8.8×10^{-6}	[74]
UV-VIS	Kolorymetria	Gazowa	1.2×10^{-8} – 5.2×10^{-7} 2.9×10^{-7} – 2.6×10^{-6}	2.06×10^{-8}	[37]

SPE/PAA	SWV	Gazowa	$7.3 \times 10^{-11} - 7.3 \times 10^{-9}$	4.2×10^{-9}	[66]
Ti ₃ C ₂ T _x MXene/FCN-SPCE	CV	Gazowa	$1.47 \times 10^{-8} - 8.82 \times 10^{-7}$	1.2×10^{-10}	[75]
NiCo ₂ Se ₄ /GC	SWV	Gazowa	$1.22 \times 10^{-11} - 6.1 \times 10^{-11}$	---	[76]
SPE/PAA	SWV	Gazowa	$3.7 \times 10^{-11} - 3.7 \times 10^{-10}$	5.6×10^{-12}	[63]
PB-SPE/ PAA	SWV	Wodna	$1 \times 10^{-5} - 1 \times 10^{-3}$	2.3×10^{-6}	[71]
PB-SPE/ PAA	SWV	Gazowa	$3.7 \times 10^{-12} - 1.85 \times 10^{-9}$	---	[71]
PB-SPE/ pAMPS	SWV	Gazowa	$3.7 \times 10^{-11} - 3.7 \times 10^{-10}$	8.7×10^{-12}	[72]
TPh-GC rod	SWV	Gazowa	$1.85 \times 10^{-12} - 2.96 \times 10^{-11}$	1.3×10^{-13}	[77]
TPh-GC rod	EFS	Gazowa	$3.7 \times 10^{-13} - 3.7 \times 10^{-12}$	7.8×10^{-14}	[77]
TPh-GC rod	DSWV	Gazowa	$3.7 \times 10^{-14} - 3.7 \times 10^{-13}$	2.8×10^{-15}	[77]

CL – chemiluminescencja, HRP/BSA - peroksydaza chrzanowa/albumina surowicy bydlęcej, PhC - kryształ fotoniczny. Kolorem zielonym zaznaczono wyniki uzyskane w ramach niniejszej rozprawy doktorskiej.

Najważniejsze osiągnięcia naukowe

Celem przeprowadzonych w ramach niniejszej dysertacji badań było opracowanie nowych metod elektrochemicznej detekcji gazowego nadtlenu wodoru z wykorzystaniem układu katalitycznego jonów miedzi(II) oraz określenie czynników wpływających na ich właściwości analityczne. Zakres badań obejmował zarówno analizę mechanizmów elektrokatalitycznych zachodzących w układach zawierających jony miedzi(II) oraz wybrane polielektrolity, a także rozwój nowych konfiguracji pomiarowych przeznaczonych do oznaczania H₂O₂ w fazie gazowej.

W pierwszym etapie badań potwierdziłem, iż obecność kwasu poliakrylowego prowadzi do stabilizacji pośrednich jonów Cu^+ , wpływając na ich dostępność w środowisku wodnym, tym samym zmieniając przebieg procesów redoks i wzmacniając właściwości elektrokatalityczne układu $\text{Cu}^{2+}/\text{Cu}^+$ względem redukcji H_2O_2 . Otrzymane wyniki pozwoliły na wyjaśnienie mechanizmów odpowiedzialnych za generowanie odpowiedzi elektrochemicznej oraz stworzyły podstawy do opracowania pierwszego układu do elektrochemicznej detekcji gazowego H_2O_2 wykorzystującego połączenie PAA i jonów Cu^{2+} .

W kolejnych badaniach skoncentrowałem się na kompleksowej charakterystyce komercyjnie dostępnych elektrod sitodrukowanych oraz określeniu wpływu ftalocyjny kobaltu(II) i błękitu pruskiego jako modyfikatorów ich powierzchni aktywnej na właściwości detekcji. Przeprowadzone porównanie wykazało istotny wpływ rodzaju zastosowanego modyfikatora na przebieg procesów elektrokatalitycznych oraz możliwości detekcji nadtlenu wodoru. Kluczowym aspektem badań było zaobserwowanie wyraźnego efektu synergistycznego pomiędzy błękitem pruskim a jonami miedzi(II), prowadzącego do amplifikacji rejestrowanego sygnału związanego z redukcją nadtlenu wodoru. Efekt ten umożliwił poprawę parametrów detekcyjnych opracowanego sensora oraz wskazał na możliwość wykorzystania połączenia klasycznego modyfikatora powierzchni elektrody z rozpuszczalnym mediatorem redoks jako nowej strategii projektowania układów zdolnych do oznaczania śladowych ilości gazowego nadtlenu wodoru. Jednocześnie zaobserwowane zależności stworzyły podstawy do opracowania pośredniej metody detekcji H_2O_2 bazujące na wspomnianym efekcie synergistycznym.

W następnej części badań wykazałem, że rodzaj zastosowanego polielektrolitu w istotny sposób wpływa na przebieg procesów elektrokatalitycznych oraz możliwości detekcji gazowego nadtlenu wodoru. Szczególnie korzystne właściwości uzyskałem dla układów opartych na pAMPS oraz pAAmAA, przy czym najlepsze rezultaty zaobserwowałem dla pAMPS o pH 2. Zastosowanie tego polielektrolitu umożliwiło poprawę czułości i powtarzalności opracowanego układu analitycznego.

Do najważniejszych osiągnięć niniejszej rozprawy doktorskiej zaliczam opracowanie nowego układu pomiarowego wykorzystującego granicę trzech faz, umożliwiającego bezpośrednią detekcję gazowego nadtlenu wodoru. Zastosowanie tej konfiguracji poprawiło transport gazowego analitu do powierzchni elektrody, skróciło całkowity czas analizy oraz pozwoliło na znaczne obniżenie granicy wykrywalności. Ponadto, połączenie układu trójfazowego z zaawansowanymi technikami

elektrochemicznymi umożliwiło jeszcze większe obniżenie granicy wykrywalności gazowego nadtlenu wodoru, osiągając LOD rzędu 10^{-15} mol L⁻¹.

Całość przeprowadzonych przeze mnie badań doprowadziła do przygotowania kilku nowych strategii oznaczania gazowego nadtlenu wodoru, charakteryzujących się wysoką czułością, dobrą powtarzalnością oraz możliwością prowadzenia badań w czasie rzeczywistym. Wyniki badań zostały opracowane w postaci czterech artykułów naukowych w recenzowanych czasopismach znajdujących się na liście filadelfijskiej. Moja praca przyczyniła się do poszerzenia wiedzy dotyczącej elektrochemicznych mechanizmów detekcji H₂O₂ oraz dostarczyła nowych rozwiązań mogących znaleźć zastosowanie w konstrukcji wysoko czułych sensorów gazowych. Tym samym zrealizowałem wszystkie cele naukowe założone w ramach niniejszej dysertacji.

Publikacje naukowe stanowiące podstawę niniejszej rozprawy doktorskiej:

- N. Ullah, D. Guziejewski, B. Barton, V. Mirceski, Electrocatalytic reduction of hydrogen peroxide in solution in the presence of polyacrylic acid and copper ions: Application for gaseous hydrogen peroxide detection, *Journal of Electroanalytical Chemistry*, 951 (2023) 117918.
- B. Barton, N. Ullah, D. Guziejewski, P. Krzyczmonik, V. Jovanovski, V. Mirceski, Detection of gaseous hydrogen peroxide using polyacrylic acid–copper(II) catalytic system at carbon-based screen-printed electrodes, *Ionics*, 31 (2025) 12245-12256.
- B. Barton, N. Ullah, V. Mirceski, S. Smarzewska, K. Koszelska, V. Jovanovski, D. Guziejewski, Polyelectrolyte-Enhanced Electrochemical Sensing of Gaseous Hydrogen Peroxide With Copper(II)–Mediating Systems, *Electroanalysis*, 38 (2026) e70113.
- B. Barton, N. Ullah, V. Mirceski, D. Guziejewski Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface; in *Microchemical Journal* (w recenzji w czasopiśmie *Microchemical Journal*)

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Udział w projektach naukowo-badawczych

- 2022-2025, Stypendysta projektu NCN OPUS LAP 20 Nr 2020/39/I/ST4/01854 „Elektrochemiczne sensory gazowe do detekcji nadtlenu wodoru”

Odbyte staże naukowe

- Staż naukowy zrealizowany na Uniwersytecie Świętego Cyryla i Metodego w Skopje, Macedonia, finansowany w ramach projektu NAWA PROM Międzynarodowa wymiana stypendialna doktorantów i kadry akademickiej (26.04.2023 - 08.05.2023)

- Staż naukowy zrealizowany w Narodowym Instytucie Chemii w Lublanie, Słowenia, finansowany w ramach projektu NAWA PROM Międzynarodowa wymiana stypendialna doktorantów i kadry akademickiej (07.05.2025 - 03.06.2025)

Odbyte szkoły letnie

- Szkoła letnia International Summer School "Food Safety and Healthy living (Session 2) FSHL2 - 2023", Lublana, Słowenia (15.09.2023 - 23.09.2023)
- Szkoła letnia "Summer School of Hazardous Substances", Lublana, Słowenia (06.05.2024 - 23.05.2024)
- Szkoła letnia "Certified Reference Materials for the Quality of Chemical Measurements: Production and Application of CRMs in Research Laboratory", Warszawa, Polska (28.07.2024 - 03.08.2024)

Spis wystąpień konferencyjnych

Wystąpienia konferencyjne ustne

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Organizacja konferencji naukowych

- Członek komitetu organizacyjnego IV Konferencji Naukowej Studentów "Młodzi Zdolni", 2023, 02.06.2023, Łódź, Polska
- Członek komitetu organizacyjnego V Konferencji Naukowej Studentów "Młodzi Zdolni", 2026, 10.04.2026, Łódź, Polska

Pozostałe aktywności naukowe

- Czynny udział w organizacji Dnia Otwartego Wydziału Chemii UŁ 2025
- Czynny udział w organizacji Dnia Otwartego Wydziału Chemii UŁ 2026

**Publikacje stanowiące
podstawę rozprawy
doktorskiej**



Electrocatalytic reduction of hydrogen peroxide in solution in the presence of polyacrylic acid and copper ions: Application for gaseous hydrogen peroxide detection

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ARTICLE INFO

Keywords:

Electrocatalytic reduction of hydrogen peroxide
Polyacrylic acid
Copper ions
Square-wave voltammetry

ABSTRACT

A comprehensive voltammetric investigation into the electrocatalytic electrode mechanism for the reduction of hydrogen peroxide in an aqueous polyacrylic acid solution, in the presence of Cu^{2+} ions, is presented. The primary objective is to lay the groundwork for the development of a straightforward electrochemical sensor for the detection of gaseous H_2O_2 . Various electrode reaction pathways have been observed depending on the potential applied to the glassy carbon electrode. At potentials approximately -0.400 V vs. Ag/AgCl (3 mol L^{-1} KCl), an electrochemical reduction of H_2O_2 occurs. In this context, the $\text{Cu}^{2+}/\text{Cu}^+$ redox couple, stabilized by polyacrylic acid, acts as a redox mediator, following the EC' reaction scheme. Additionally, a complex Fenton-like spontaneous redox chemistry takes place between $\text{Cu}^{2+}/\text{Cu}^+$ and H_2O_2 within the bulk of the polyacrylic aqueous solution. This results in the generation of a variety of reactive oxygen species (ROS), with the superoxide anion and hydroxyl radical being the most probable intermediates. The electrochemical reduction of ROS species effectively recycles H_2O_2 near the electrode surface, constituting an electrocatalytic mechanism of the second order. This particular electrocatalytic process is evident as a prominent reduction current tail at potentials more negative than -0.400 V. This, in conjunction with the adsorption and stabilizing influence of polyacrylic acid, facilitates exceptional analytical sensitivity for the detection of gaseous H_2O_2 . The sensor exhibits the capability to detect concentrations of gaseous H_2O_2 as low as $10^{-11} \text{ mol L}^{-1}$, accomplished through the utilization of square-wave voltammetry and other advanced voltammetric techniques.

1. Introduction

Hydrogen peroxide (H_2O_2), as an intermediate and/or byproduct of numerous metabolic reactions, is an important biomolecule. Its reliable detection and quantification are of utmost importance for understanding a variety of biochemical and physiological pathways. Quantitative measurements of gaseous hydrogen peroxide concentration are useful for diagnosing serious diseases, such as asthma, and lung cancer, [1–3]. The concentration irregularity of hydrogen peroxide in a gas phase, e.g. in exhaled breath, is an indicator for other diseases such as diabetes, heart diseases, neurodegenerative conditions, acute respiratory distress syndrome (ARDS), chronic obstructive pulmonary disease (COPD), and cystic fibrosis (CF) [4–11]. Besides biochemistry, the detection of H_2O_2 is the focus of research due to security reasons, as it is a component of

homemade peroxo-explosive materials (diacetone diperoxide and triacetone triperoxide), which have been associated with recent terrorist attacks [12–14]. A simple and fast detection of these volatile explosives seems to be possible only through H_2O_2 detection in the gas phase, which imposes an additional challenge for the electrochemical research of H_2O_2 . In addition, gaseous H_2O_2 is recognized as a pivotal molecule in various atmospheric processes, being a product of chemical transformation of primary and secondary organic aerosols [15]. In the vast field of analytical chemistry of H_2O_2 , a range of techniques have been applied, such as chromatography [16], fluorescence [17], chemiluminescence [18], colorimetry [19], and electrochemical [20,21], to mention just a few. Among these methods, electrochemical techniques have gained extensive attention due to their simplicity and sensitivity [22,23]. Available electrochemical methods for H_2O_2 gas detection are

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<https://doi.org/10.1016/j.jelechem.2023.117918>

Received 23 September 2023; Received in revised form 24 October 2023; Accepted 6 November 2023

Available online 14 November 2023

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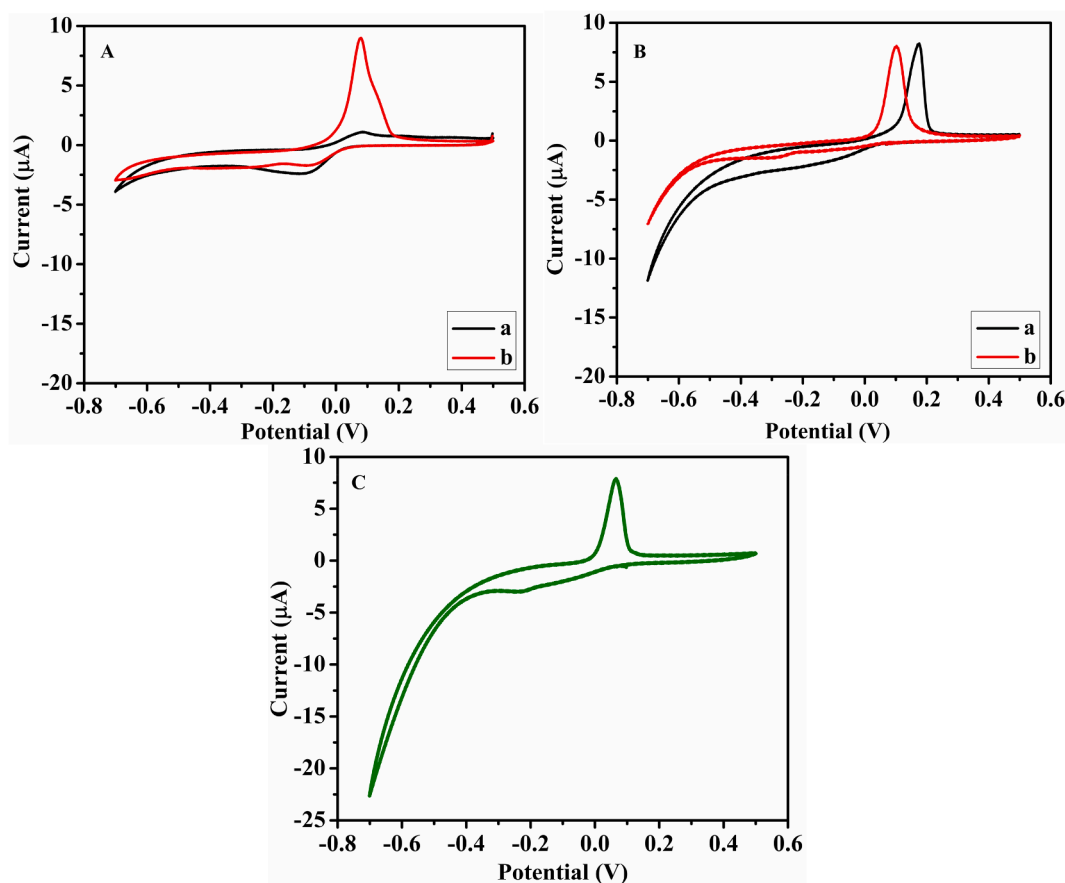


Fig. 1. (A) Cyclic voltammograms of 2×10^{-4} mol L $^{-1}$ Cu $^{2+}$ in supporting electrolyte of 0.1 M KNO $_3$ in the presence of O $_2$ (a) and after degassing the solution (b). (B) Cyclic voltammograms of 2×10^{-4} mol L $^{-1}$ Cu $^{2+}$ in the supporting electrolyte of 0.1 M KNO $_3$ containing 1 % PAA in the presence of O $_2$ (a) and after degassing of the solution (b). (C) Cyclic voltammograms of 2×10^{-4} mol L $^{-1}$ Cu $^{2+}$ in the supporting electrolyte of 0.1 M KNO $_3$ and 1 % PAA in the presence of 2×10^{-3} mol L $^{-1}$ H $_2$ O $_2$ in presence of O $_2$. The scan rate for all voltammograms is 50 mV s $^{-1}$.

scarce, Kuwata and Sadaoka [24], detect hydrogen peroxide in air directly on amperometric sensor cell (cathode Au/Nafion/Pt anode), which show linear response to H $_2$ O $_2$ increment in air. Similarly, Hocevar and his group have developed several sensors [25–28] including a sensor for gaseous hydrogen peroxide [8]. The sensor detects hydrogen peroxide in the air as real sample, after the room was disinfected with 10 % H $_2$ O $_2$ solution.

Selection of an appropriate medium is clearly of crucial importance in H $_2$ O $_2$ gas detection using electrochemical techniques. The excellent features of polyacrylic acid (PAA), such as its polyelectrolytic capability [29], high water absorbency [30], superior biocompatibility [31], and ability to form thin films [32], make it an appealing medium for H $_2$ O $_2$ detection. Moreover, recalling that the features of PAA can be controlled by the degree of cross-linking by means of temperature, ionic strength, type and concentration of counter ions, and pH [33,34], the versatile physicochemical characteristics of PAA make it a tempting medium for the preparation of electrochemical sensors [35]. In addition to the requirements for a specific medium selection, electrochemical detection of H $_2$ O $_2$ often requires an electrocatalyst or a redox mediator due to the known sluggish electrode kinetics and complex electrode mechanism [36]. Various species have been employed as electrocatalysts, including enzymes [37], polymeric sensing membranes [38], nanoparticles of metals and metal oxides [22,39], and carbon-based nanoparticles [40]. Among these materials, copper nanoparticles gained special attention due to their excellent electrocatalytic activity, low cost, and biocompatibility [3,41–46].

In a recent study, we conducted an investigation into the electrode mechanism of Cu $^{2+}$ (aq) reduction in aqueous PAA solutions to establish

a foundation for H $_2$ O $_2$ detection [47]. Our findings demonstrated that Cu $^{+}$ acts as a redox mediator during the electrode reduction of Cu $^{2+}$ to metallic Cu(s), enabling electrochemical detection of H $_2$ O $_2$ [48–50]. However, a previous study suggested that the Cu $^{2+}$ -PAA- H $_2$ O $_2$ system exhibits even more remarkable electrocatalytic properties in the potential region where Cu(s) species are present, either immobilized on the electrode surface or dispersed near it. Consequently, the present study focuses on the electrochemical reduction of H $_2$ O $_2$ on a Cu(s)-modified electrode in an aqueous PAA solution, elucidating mechanistic aspects of the electrode reaction, with the aim of establishing a novel method for H $_2$ O $_2$ detection in the gas phase. In addition to conventional cyclic voltammetry (CV) and square-wave voltammetry (SWV), advanced variants of SWV, including square-wave chronoamperometry (SWC) (also known as electrochemical faradic spectroscopy) [51,52], and differential square-wave voltammetry (DSWV) [53,54], have been employed for analytical purposes. It is worth noting that this study marks the first application of SWC and DSWV in electrochemical detection of H $_2$ O $_2$.

2. Experimental

All chemicals used were purchased from Sigma-Aldrich and were of analytical grade. They were used without any further purification. Deionized water (DI water) obtained from the Polwater DL-3 purification system was used to prepare all stock solutions. Stock solutions of KNO $_3$ (0.1 mol L $^{-1}$), CuSO $_4$ (0.1 mol L $^{-1}$), and H $_2$ O $_2$ (0.1 mol L $^{-1}$) were prepared. Non-cross-linked PAA with a molar mass of 450,000 g/mol was used for the PAA solution; 1 g of PAA was added to 100 mL of KNO $_3$

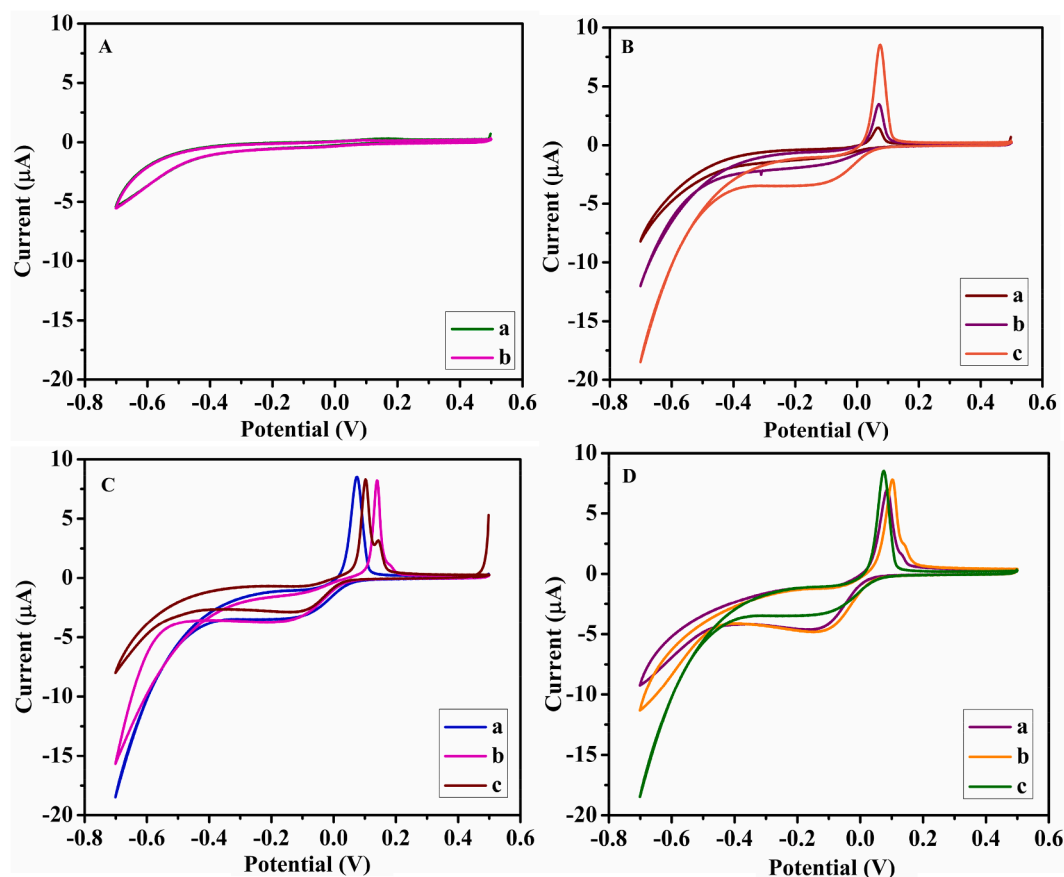


Fig. 2. (A) Cyclic voltammograms of 1 % aqueous solution of PAA and 0.1 mol L⁻¹ aqueous KNO₃ solution in absence of H₂O₂ (a) and in presence of 2×10^{-3} mol L⁻¹ H₂O₂ (b). (B) Cyclic voltammograms of 2×10^{-3} mol L⁻¹ H₂O₂ in the supporting electrolyte 0.1 mol L⁻¹ KNO₃ and 1 % PAA, containing Cu²⁺(aq) ions at concentration of 5×10^{-5} (a); 1×10^{-4} (b) and 2×10^{-4} mol L⁻¹ Cu²⁺ (c). (C) Cyclic voltammogram of 2×10^{-3} mol L⁻¹ H₂O₂ in the presence of 2×10^{-4} mol L⁻¹ Cu²⁺ in unbuffered 0.1 mol L⁻¹ KNO₃ solution containing 1 % of PAA (a) and in solutions additionally containing Britton-Robinson buffer at pH of 2 (b) and 4 (c). (D) Cyclic voltammograms of 2×10^{-3} mol L⁻¹ H₂O₂ in 0.1 mol L⁻¹ KNO₃ solution containing 2×10^{-4} mol L⁻¹ Cu²⁺ and PAA at mass percentage of 0.1 (a); 0.5 (b) and 1 % of (c).

(0.1 mol L⁻¹) as a supporting electrolyte to create a 1 % stock solution with a pH value of 2.9. Additionally, a Britton-Robinson buffer solution was used to assess the effect of pH.

The electrochemical study was conducted using a three-electrode system, where glassy carbon (GC), Ag/AgCl (3 mol L⁻¹ KCl), and Pt electrodes were employed as the working, reference, and auxiliary electrodes, respectively. The working electrode was cleaned with Al₂O₃ slurry, rinsed with deionized water, and dried on air before each experimental step. Unless otherwise specified, the study was carried out at room temperature in the presence of oxygen. In order to investigate the influence of oxygen, a series of experiments were conducted in deoxygenated solutions, as clearly indicated in the titles of the corresponding figures.

The study for the detection of gaseous H₂O₂ was conducted in a closed glass bottle chamber with a total volume of 1 L. Screen-printed electrode (SPE) strips (Metrohm DropSens, 110) were used as an electrochemical sensor. The SPE strips were printed with Ag and carbon, serving as quasi-reference, working, and auxiliary electrodes, respectively. A 50 mL of aqueous H₂O₂ solution with a concentration ranging from 1×10^{-4} to 1×10^{-2} mol L⁻¹ was placed in the chamber. The H₂O₂ aqueous solution was left for 3 h to establish equilibrium between the gas and liquid phases before collecting electrochemical data. According to Henry's law [55,56], the concentration of H₂O₂ in the gas phase was estimated to range from 6.1×10^{-11} to 4.2×10^{-9} mol L⁻¹.

Following equilibration of the phases, the SPE strip was coated with a 50 μL solution containing 2×10^{-4} mol L⁻¹ Cu²⁺(aq), 0.1 mol L⁻¹ KNO₃ and 1 % PAA to fully cover all three electrodes of the strip. The coated

strip was then introduced into a well-saturated environment with gaseous H₂O₂ inside the chamber and kept for 3 min to allow the dissolution of gaseous H₂O₂ in the targeted solution on the SPE. Experiments with different incubation time of 1, 2, 3, 4, 5 min were performed for optimization, where the results corresponding to 1 and 2 min were not reproducible, while the response following 3, 4, and 5 min incubation was almost identical.

All electrochemical sensing measurements were collected using multi-channel m-Autolab potentiostat, controlled by the Nova (v. 2.1.4) software (Metrohm Autolab B.V.).

3. Results

3.1. Electrochemical characterisation

Typical cyclic voltammograms of 2×10^{-4} mol L⁻¹ Cu²⁺ at a bare GC electrode in KNO₃ aqueous solution in the presence of oxygen and in a degassed solution, are presented in Fig. 1A. Apart from the typical cathodic peak at around -0.100 V, representing the reduction of Cu²⁺(aq) to Cu(s), the voltammograms exhibit an anodic stripping peak at approximately 0.130 V. On the negative potential side, no significant oxygen reduction occurs at copper modified electrode (compare curves a and b in Fig. 1A); yet, the anodic stripping peak is diminished in the presence of oxygen (Fig. 1A), implying that oxygen impedes the electrochemical deposition of Cu(s) and alter the overall electrochemical mechanism. A careful inspection of the cathodic peak at -0.100 V reveal a sort of catalytic (redox regenerative EC' mechanism) [57–59] in the

presence of oxygen, implying that the intermediate $\text{Cu}^+(\text{aq})$ ions are involved in a redox reaction with oxygen to form $\text{Cu}^{2+}(\text{aq})$ and hydrogen peroxide [60].

To further the experiment, the KNO_3 aqueous supporting electrolyte was supplemented with 1 % PAA (Fig. 1B). In the absence of oxygen (curve **b** in Fig. 1B), the cathodic part of the cyclic voltammogram exhibits similarities to that observed in the pure aqueous KNO_3 solution (Fig. 1A, curve **b**). However, the anodic stripping peak shows a well-defined, less complex morphology compared to that in KNO_3 . This indicates the formation of a uniform metallic deposit on the electrode surface in the presence of PAA, implying interactions between PAA and copper species, particularly the stabilization of $\text{Cu}^+(\text{aq})$ species, as demonstrated in our previous study [47]. In the presence of oxygen the electrocatalytic effect is even more effective at potential of -0.100 V in PAA containing solution, which has features of the regenerative EC' catalytic mechanism, as in the absence of PAA (compare curves **a** in Fig. 1A and B). More importantly, in the presence of oxygen an intensive cathodic tail emerges at potentials more negative than -0.400 V (curve **a** in Fig. 1B), associated with a new, reductive catalytic process. At the same time, the anodic stripping peak shifts toward more positive potentials confirming that oxygen affects the overall electrochemical process of copper.

In the presence of H_2O_2 and oxygen in the PAA containing supporting electrolyte (Fig. 1C), the reduction tail increases dramatically (by approximately $10 \mu\text{A}$ measured at the limiting potential of -0.700 V), revealing that the same catalytic process observed with O_2 proceeds at significantly higher rate when H_2O_2 is deliberately added to the solution. It is also important to note that during the reverse potential scan, the voltammetric curve virtually follows the same path of the forward cathodic tail (Fig. 1C). Moreover, under certain conditions, the reverse voltammetric component could be associated even with stronger cathodic currents, being shifted towards more positive potentials and intersecting the forward voltammetric curve at potentials around -0.400 V (vide infra). The data in Fig. 1 reveal important aspect of the complex electrochemistry of the system Cu^{2+} -PAA- O_2 - H_2O_2 . The EC' reaction scheme, between Cu^+ and O_2 is obviously valid in the presence and in the absence of PAA. Yet, PAA stabilizes one of the products of these reaction scheme, i.e., H_2O_2 , which is further involved in additional electrocatalytic mechanism at potentials more negative than -0.400 V (compare curve **b** in Fig. 1B and Fig. 1C).

To investigate the role of copper in the overall electrocatalytic process, typical cyclic voltammograms for the reduction of H_2O_2 in the absence and the presence of copper are presented in 2A and 2B, respectively. In Fig. 2A, it is evident that H_2O_2 does not undergo electrochemical reduction in the absence of $\text{Cu}^{2+}(\text{aq})$, even in a KNO_3 and PAA aqueous solution. Conversely, Fig. 2B demonstrates the pronounced electrocatalytic effect of copper, which is directly proportional to the concentration of $\text{Cu}^{2+}(\text{aq})$ [45]. This effect is observed in terms of the increased intensity of the cathodic current at potentials close to -0.100 V (i.e., reduction of Cu^{2+} to $\text{Cu}(\text{s})$ via the intermediate Cu^+ [61]), as well as at potentials more negative than -0.400 V. Obviously, the redox chemistry of H_2O_2 and both Cu^+ and Cu^{2+} is of critical importance form the overall voltammetric features in PAA containing solutions [47].

Since the state of PAA and the redox chemistry of H_2O_2 are both highly sensitive to pH [34], reduction of H_2O_2 in the PAA containing solution was investigated in the presence of a buffer (Fig. 2C). Note that the electrolytic solution consisting of 1 % PAA in a $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ solution has a pH of 2.9, indicating that a small portion of PAA is in a deprotonated form. According to literature data, $\text{Cu}^{2+}(\text{aq})$ predominantly exists in form of aqua-complex, while approximately 10 % of the total concentration is complexed with carboxylic groups of PAA [62]. In a buffered acidic medium with a pH of 2, the cathodic tail starts to develop at more negative potentials compared to the unbuffered solution (compare curve **a** and **b** in Fig. 2C). Moreover, the reverse voltammetric curve exhibits peculiar behaviour by intersecting the forward

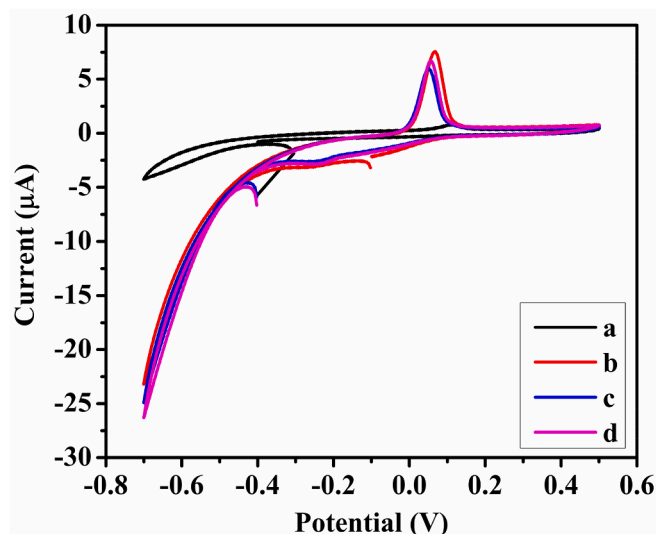


Fig. 3. The role of deposition protocol in cyclic voltammetry. (a) The deposition of copper has been performed in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ solution containing $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ and 1 % PAA at potential of -0.400 V for 10 s. Then, the modified electrode was immersed into $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ solution containing 1 % PAA and $2 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, free of copper ions; (b) Cyclic voltammogram recorded at starting potential of -0.100 V with the first vertex potential of -0.700 V and the second vertex at 0.500 V in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ solution containing $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$, 1 % PAA, and $2 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$; (c) Cyclic voltammogram recorded by deposition at -0.400 V for 10 s. The initial potential is identical with the deposition potential; the first and second vertex potentials, together with other conditions are identical as for curve (b); (d) Cyclic voltammogram recorded at starting potential of -0.400 V without deposition. The rest of the conditions are identical as for curve (b).

voltammetric curve at potentials around -0.400 V. Importantly, the maximum cathodic current at the limiting potential of -0.700 V is lower at pH = 2 than in unbuffered solution at pH = 2.9. Additionally, at pH 2, the anodic stripping peak is shifted to a more positive potential of about 70 mV compared to the unbuffered solution. These data clearly indicate that voltammetric features manifested as a cathodic current tail at potentials more negative than -0.400 V are not related to the catalytic proton reduction, rather to the complex electrocatalysis of H_2O_2 in the presence of copper species.

The system was also studied in a buffer with a pH of 4. In this case, the anodic peak shifted positively by only 27 mV, while the evolution of the reduction tail was shifted by approximately 144 mV towards more negative potentials (compare curves **a** and **c** in Fig. 2C). The peculiar pH effect does not solely originate from the role of PAA but also from the pH sensitivity of the overall electrode mechanism, which likely involves a multitude redox reactions between H_2O_2 and copper species, resulting in formation of various oxygen-containing radical species [49]. Despite the complexity of the electrochemical mechanism, the response in the unbuffered PAA solution seems to be the most promising from an empirical and analytical perspective.

Besides copper ions, the electrocatalytic effect depends significantly on the PAA concentration, as demonstrated in Fig. 2D, which displays voltammograms obtained in solutions containing 0.1, 0.5, and 1 % PAA. The intensity of the electrocatalytic effect is directly proportional to the PAA concentration. Furthermore, it appears that the morphology of the $\text{Cu}(\text{s})$ deposit is also influenced by the PAA content. This is evident from the characteristics of the copper anodic stripping peak, which increases in proportion to the PAA content, while in the presence of 1 % PAA, exhibits a sharp and uniform anodic peak. This peak is slightly shifted towards less positive potentials, approximately by 40 mV, compared to the 0.1 % PAA solution (compare curves **a** and **c** in Fig. 2D). Clearly, PAA favours formation of a uniform metallic copper film on the electrode surface. By comparing the data from panels 2A, B, and D, it can be

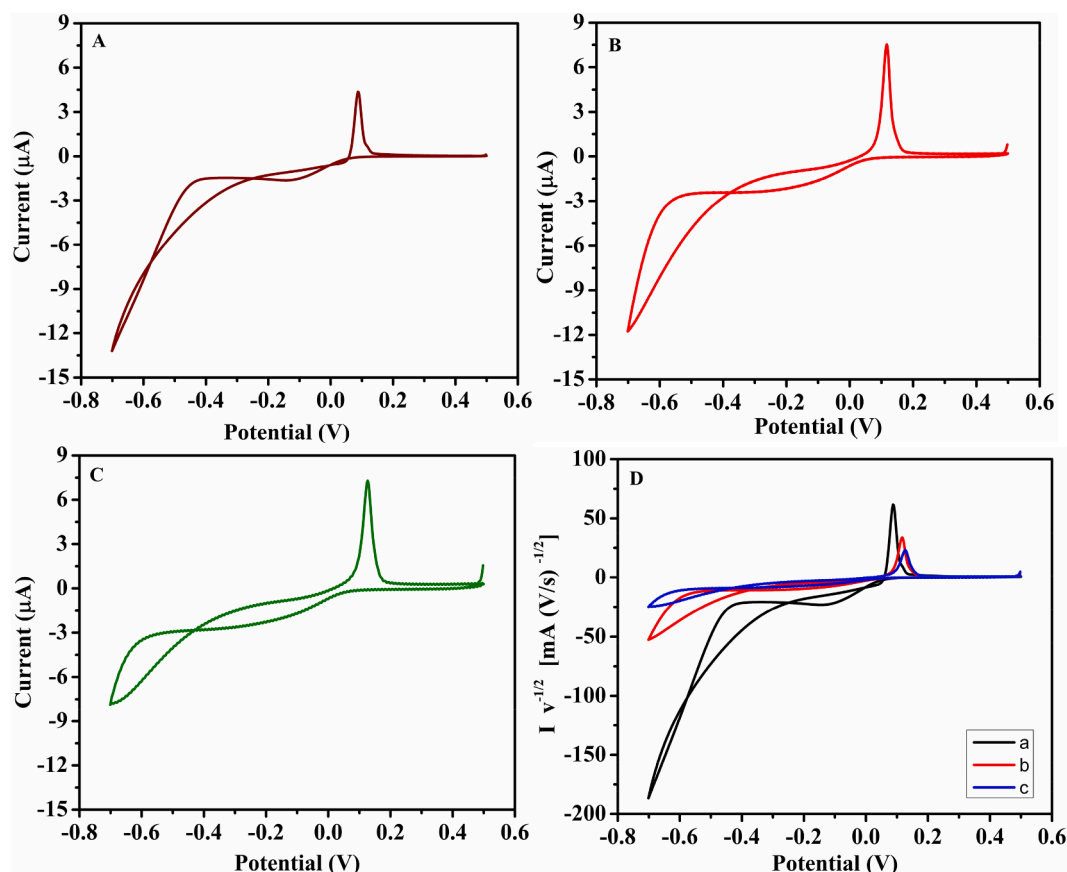


Fig. 4. Cyclic voltammogram of $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ in supporting electrolyte of 0.1 M KNO_3 , 1 % of PAA and $2 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ at scan rate of 5 (A), 50 (B), and 100 mV s^{-1} (C). Panel D compares scan rate normalized voltammograms for the same scan rate values of 5 (a); 50 (b) and 100 mV s^{-1} (c).

deduced that the electrocatalytic effect of PAA is primarily observed through its impact on copper species [63] rather than through a direct effect on the electrochemical reduction of H_2O_2 , which practically does not take place in the absence of copper ions (curve **a** in Fig. 2A).

To uncover whether metallic copper deposit (Cu(s)) on the electrode surface or the copper nanoparticles ($\text{Cu}^0(\text{aq})$), formed by the disproportionation of the $\text{Cu}^+(\text{aq})$ intermediate [64], are the actual electrocatalyst, a systematic analysis of the deposition time and potential has been conducted and representative voltammograms are depicted in Fig. 3. Curve **a** in Fig. 3 corresponds to the experiment in which the deposition of copper has been conducted in a H_2O_2 free solution. Afterwards, the copper modified electrode has been transferred into H_2O_2 containing solution free of copper ions, and the voltammetry was commenced from -0.400 V in a negative potential direction. Note that at -0.400 V no electrochemical oxidation of metallic copper takes place and no copper ions are electrochemically formed in the vicinity of the electrode. Intriguingly, virtually no cathodic tail was observed sweeping the potential from -0.400 to -0.700 V , pointing clearly that the direct reduction of H_2O_2 via the metallic copper deposit (Cu(s)) is virtually insignificant.

In addition, voltammograms **b-d** in Fig. 3 are recorded in solutions containing both $\text{Cu}^{2+}(\text{aq})$ and H_2O_2 , initiating the voltammetry at -0.100 V (curve **b**), at -0.400 V (curve **c**), and by previous incubation of the electrode for 10 s at the initial potential of -0.400 V (curve **d**). The cathodic tail is obviously independent on both the initial potential and incubation time (i.e., deposition time). The experiment corresponding to curve **b** plausibly includes sequential reduction of $\text{Cu}^{2+}(\text{aq})$ to Cu(s) via disproportionation of $\text{Cu}^+(\text{aq})$ intermediate, thus resulting in Cu(s) in the form of both metal deposit (Cu(s)) and metal nanoparticles in the diffusion layer ($\text{Cu}^0(\text{aq})$) [47,65]. Voltammograms recorded from -0.400 V (curves **c** and **d**), in particular the experiment including

deposition time (curve **d**), favour predominantly electrochemical formation of metallic copper deposit on the electrode surface (Cu(s)). Yet, in all three cases, the cathodic tail is identical, implying that elemental copper species, either on the electrode surface or in the vicinity of the electrode, are not critical in the overall electrocatalytic mechanism. Thus, in agreement with previous conclusion, the redox chemistry undergoing in solution between H_2O_2 and copper species gives rise to the reduction tail at potentials more negative than -0.400 V . Importantly, the intensity of the reduction current tail is independent on the amount of copper deposit on the electrode surface, implying that the electrode reaction predominantly takes place on the bare electrode surface.

The effect of the potential scan rate (v) sheds additional light to the electrode mechanism, as illustrated in Fig. 4. The scan rate exhibits a profound effect on the morphology of the voltammetric curves, in particular in the potential region of our interest, i.e., more negative than -0.400 V . Interestingly, the maximum cathodic current at the limiting potential of -0.700 V depends inversely on the scan rate, implying that the electrode reaction is not diffusion controlled, rather than it is gated by the kinetics of a chemical reaction (Fig. 4A–C) [66]. The intersection of the reverse voltammetric curve with the forward one also depends significantly on the scan rate, shifting toward more negative potentials by increasing the scan rate. Fig. 4D compares scan rate normalized voltammograms, aiming to illustrate the intrinsic mechanistic aspect of the electrode reaction. Let us recall that the ratio $I/v^{1/2}$ represents the dimensionless current function [67], which solely depends on the electrode mechanism and avoids the effect of the diffusion layer thickness. The strong decrease of the overall current by increasing the scan rate from 5 to 100 mV s^{-1} , suggest a mechanism in which the electroactive reactant is formed in a preceded chemical reaction (i.e., a CE mechanism [57]). These data additionally support the conclusion that the reduction tail at potentials more negative than -0.400 V is due to reduction of

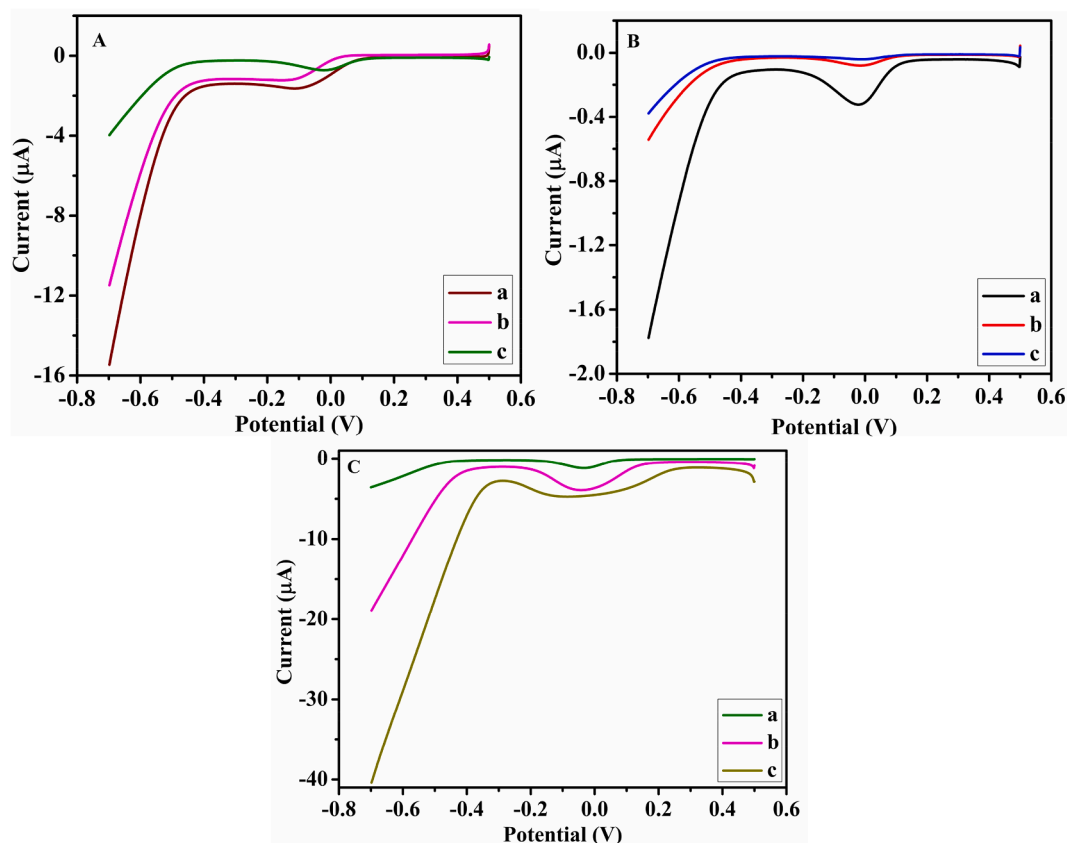
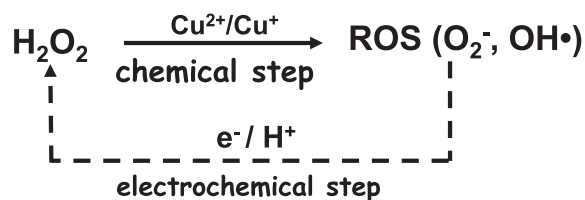


Fig. 5. (A) Typical square wave voltammetric response of $2 \times 10^{-3} \text{ mol L}^{-1}$ of H_2O_2 recorded in 0.1 mol L^{-1} KNO_3 containing 1% of PAA and $2 \times 10^{-4} \text{ mol L}^{-1}$ Cu^{2+} , showing forward (a), backward (b), and net (c) component. The parameters of the potential modulation are SW frequency of 5 Hz, amplitude 25 mV, and step potential of 2 mV. (B) Frequency normalized net SW voltammograms for the frequency of 5 (a); 50 (b), and 100 Hz (c). The other conditions are as in panel (A). (C) The effect of the SW amplitude on the net SW voltammogram, ranging from 20 (a); 100 (b), and 200 mV (c), for the SW frequency of 8 Hz. The other conditions are as in panel (A).

particular redox species that are formed in a preceding spontaneous redox reaction between H_2O_2 and copper ions [60].

Further electrochemical characterisation has been conducted by advanced technique of square-wave voltammetry. Fig. 5A depicts typical SW voltammetric response of the studied system containing both Cu^{2+} and H_2O_2 . Forward and backward voltammetric curves has a typical shape of a catalytic electrode processes [68], both in the potential region of the $\text{Cu}^{2+}(\text{aq})$ reduction (around -0.100 V) and in the region more negative than -0.400 V. The frequency analysis, represented in the form of frequency-normalized net SW voltammograms (Fig. 5B) supports the previous conclusion that the overall electrochemical mechanism is gated by the kinetics of a preceding chemical reaction [69]. Besides the SW frequency, the height of the potential pulses in SWV (i.e., SW amplitude) profoundly affects the voltammetric response. The net SW voltammograms enhance in proportion to the SW amplitude, and the effect is more pronounced in the potential region more negative than -0.400 V. Let us note that large amplitude values in the potential region more negative than -0.400 V enable electrochemical anodic dissolution of $\text{Cu}(\text{s})$ and regeneration of copper ionic species (i.e., Cu^{2+} or Cu^+) in the vicinity of the electrode in the course of the backward (anodic) potential pulses, which re-establishes the conditions for the ongoing catalytic mechanism which obviously critically depends on dissolved copper ions.

The experimental data presented suggest that the intensive reduction tail observed at potentials more negative than -0.400 V is attributed to electroactive reactants formed in a spontaneous redox reaction between $\text{Cu}^{2+}(\text{aq})$ and H_2O_2 . The electrode process generates a current tail instead of a peak-like shape, indicating a catalytic and regenerative mechanism, where the electroactive reactant is continuously



Scheme 1. The assumed reaction pathway for the electrocatalytic mechanism of a second kind giving rise to the reduction current tail at potentials more negative than -0.400 V.

replenished without diffusion limitation during voltammetry. Consistent with extensive literature data [60,70], a Fenton-like reaction involving the redox couple $\text{Cu}^{2+}/\text{Cu}^+$ and H_2O_2 is the most plausible pathway, resulting in the production of superoxide anion and hydroxyl radicals as the primary intermediates. These intermediates, stabilized by PAA [71], are considered the most likely electroactive reactants responsible for the reduction current tail. The electrochemical reduction of $\text{OH}^{\cdot}$ and/or $\text{O}_2^{\cdot-}$ leads to the formation of H_2O_2 , which in turn recycles the initial reactant (H_2O_2), completing the scheme of an electrocatalytic mechanism [72–74]. Scheme 1 summarizes the proposed reaction pathway, which represents a specific type of catalytic mechanism known as the “electrocatalysis of a second kind,” as described in our previous theoretical studies [69,75].

It is worth noting that according to research conducted by [76], as well as the study by [77], it has been observed that $(\text{Cu}^0(\text{aq}))$ nanoparticles formed near the electrode can also activate H_2O_2 , leading to similar Fenton-like redox chemistry. However, the present experimental

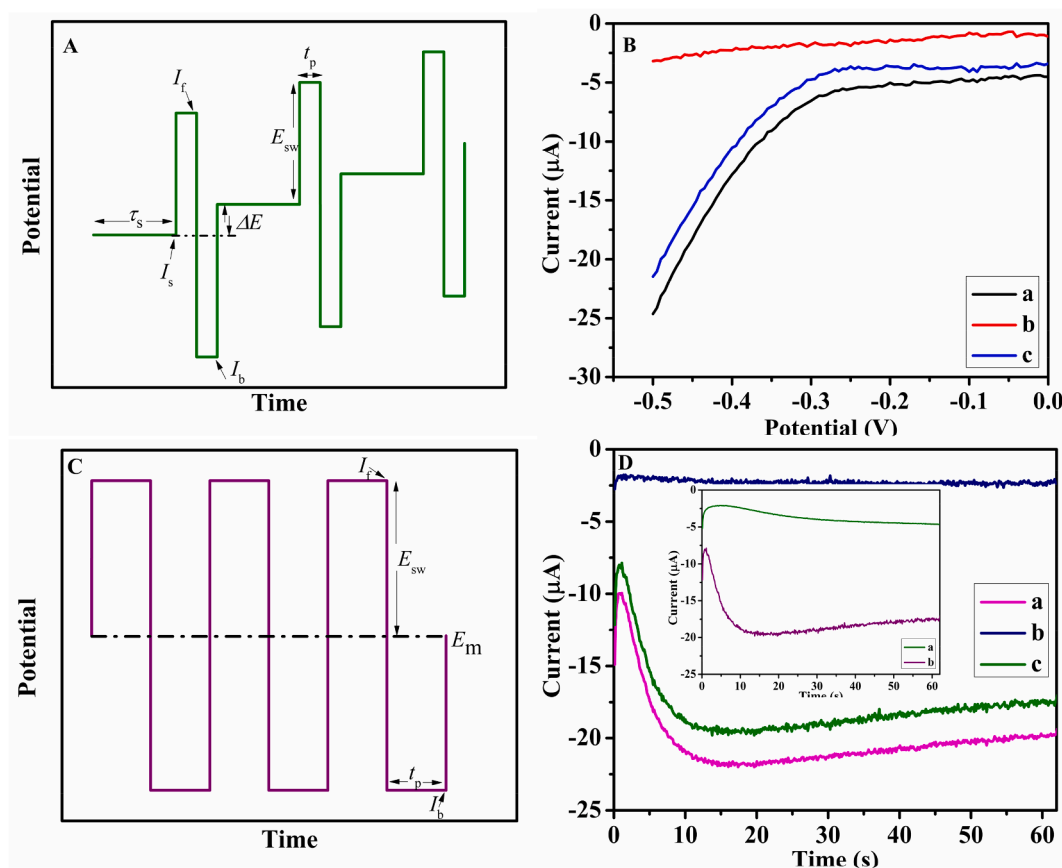


Fig. 6. (A) Potential modulation in differential square-wave voltammetry (DSWV) [53], consisting of potential steps with duration τ_s , and potential pulses with duration t_p and height E_{sw} . The step potential increment is designated as ΔE , whereas I_s , I_f , and I_b correspond to the current sampling point at the end of the potential steps (I_s), forward pulses (I_f), and backward pulses (I_b). (B) Typical DSW voltammetric response of $2 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ in 0.1 M KNO_3 electrolyte solution containing $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ and 1% of PAA, showing forward (a), backward (b), and net voltammetric component (c). The height of the pulses is $E_{sw} = 200 \text{ mV}$, frequency $f = 8 \text{ Hz}$ (i.e., $t_p = 62.5 \text{ ms}$), $\Delta E = 5 \text{ mV}$, and the step-to-pulse duration ratio is $\tau_s/t_p = 2$. (C) Potential modulation of square-wave chronoamperometry (SWC) consisting of a train of potential pulses imposed on a constant mid-potential E_m [51]. The other symbols are identical as in panel (A). (D) Typical SW chronoamperometric response of the studied system showing forward (a), backward (b) and net (c) chronoamperometric component. The experimental conditions are identical as in panel B. The inset shows classical chronoamperogram recorded at -0.450 V (a) and the net chronoamperogram of SWC recorded with $E_m = -0.450 \text{ V}$ (b).

data imply that such a process is insignificant under our experimental conditions. This conclusion is supported by the experimental data summarized in Fig. 3, where the influence of time and deposition potential was systematically investigated, enabling control over the amount of $(\text{Cu}^0(\text{aq}))$ species present.

3.2. Analytical applications

Besides SWV, an attempt has been made to use recently introduced advanced variants of SWV as an analytical tool, such as differential square-wave voltammetry (DSWV) [53] and square-wave chronoamperometry (SWC) [78]. Potential modulation waveform of DSWV, together with the typical voltammetric response of the studied system are depicted in Fig. 6A and B, respectively. Forward (a) and backward (b) voltammetric components in Fig. 6B correspond to the currents measured at the end of forward (cathodic) and backward (anodic) potential pulses, whereas the net (c) component is calculated as in the conventional SWV, i.e., $I_{\text{net}} = I_f - I_b$. The technique differs from conventional SWV in potential steps inserted between each potential cycle (Fig. 6A) consisting of two adjacent potential pulses. The overall scan rate in DSWV is lower than for SWV for a given frequency, thus the technique is more convenient for electrode processes gated by slow chemical reactions. Moreover, it is expected that DSWV would discriminate the background current more effectively than SWV [54]. In

spite of the range of advances of the technique, the voltammetric curves of the studied system in the potential region more negative than -0.400 V again appear as current tails rather than a voltammetric peak, due to the complex nature of the operative catalytic electrode mechanism.

In Fig. 6C typical potential modulation of SWC is depicted, where E_m is the mid-potential, and other parameters and current sampling protocol are identical as in conventional SWV [51]. Square-wave chronoamperometry, or alternatively termed as electrochemical Faradaic spectroscopy [79] is highly promising technique for analytical applications as it unifies the simplicity of the chronoamperometry and the advances of pulse voltammetric techniques. A typical chronoamperometric response recorded under optimized experimental conditions at mid-potential of -0.450 V is depicted in Fig. 6D, whereas the total number of potential cycles of the experiment is 500. The inset of Fig. 6D compares the classical chronoamperogram recorded at -0.450 V (curve a) and the net chronoamperogram of the SWC experiment with $E_m = -0.450 \text{ V}$. Obviously, SWC delivers more intensive response, which has obvious analytical benefits.

A detailed concentration dependency was initially carried out in a solution phase using the three techniques, i.e., SWV, DSWV and SWC, over the concentration interval of H_2O_2 from $3 \times 10^{-4} \text{ mol L}^{-1}$ to $7 \times 10^{-3} \text{ mol L}^{-1}$ ($6 \times 10^{-3} \text{ mol L}^{-1}$ in case of DSWV). The optimized supporting electrolyte consists of $0.1 \text{ mol L}^{-1} \text{ KNO}_3$, 1% PAA and $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$, whereas the instrumental parameters are SW

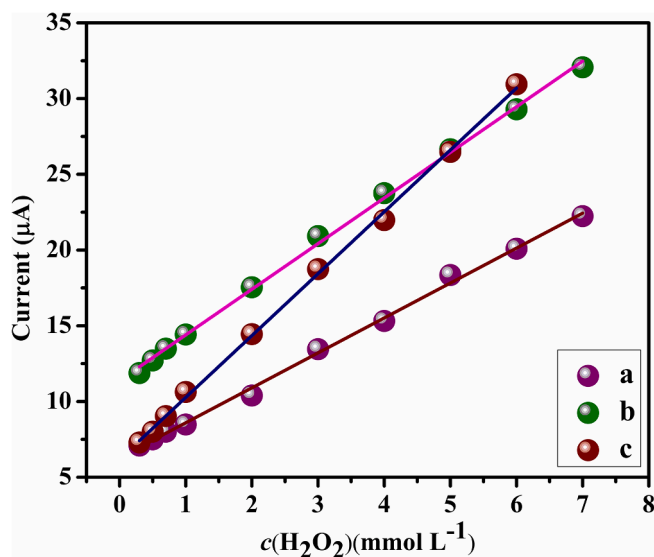


Fig. 7. Calibration curves for square-wave voltammetry (SWV) (a), square-wave chronoamperometry (SWC) (b), and differential square-wave voltammetry (DSWV) (c), over the H_2O_2 concentration interval from $3 \times 10^{-4} \text{ mol L}^{-1}$ to $7 \times 10^{-3} \text{ mol L}^{-1}$ ($6 \times 10^{-3} \text{ mol L}^{-1}$ for DSWV), in a supporting electrolyte containing 0.1 M KNO_3 , 1 % PAA, and $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}(\text{aq})$. Parameters of the potential modulations are SW frequency 8 Hz and SW amplitude 200 mV (for the three techniques), step potential 5 mV (for SWV and DSWV), and 500 potential cycles with the mid-potential of -0.450 V for SWC.

Table 1

LOD and LOQ with R^2 values for SWV, EFS, and DSWV in solution for H_2O_2 detection.

	DSWV mol L^{-1}	EFS mol L^{-1}	SWV mol L^{-1}
LOD	9.05×10^{-5}	1.17×10^{-4}	1.17×10^{-4}
LOQ	3.02×10^{-4}	3.88×10^{-4}	3.89×10^{-4}
R^2	0.9987	0.9981	0.9971

frequency 8 Hz and SW amplitude 200 mV (for the three techniques), step potential 5 mV (for SWV and DSWV), and 500 potential cycles with the mid-potential of -0.450 V for SWC. Corresponding calibration lines are depicted in Fig. 7. In SWV and DSWV the net current was measured at the fixed potential of -0.450 V , whereas in SWC, the net current is an average of the last 10 potential cycles, i.e., when the net current stabilises to a constant value [52]. The limits of detection (LOD) and quantification (LOQ), and linear regression coefficient (R^2) values for all three techniques are listed in Table 1, calculated using the standard formulas $\text{LOD} = 3 \times S_a/b$ and $\text{LOQ} = 10 \times S_a/b$, where S_a is the standard deviation of the intercept and b is the slope of the calibration line. The LOD and LOQ for SWV and SWC were found to be almost same. However, the slope of SWC of 3.0 (Fig. 7b) is higher than that for SWV, which is 2.3 (Fig. 7a). More importantly, the slope has the highest value for DSWV (4.0), implying the best sensitivity of the technique compared to SWV and SWC. Besides, LOD and LOQ are slightly lower for DSWV compared to other techniques, supporting the expected advantages of the technique [80].

Finally, the determination of H_2O_2 in a gas phase has been attempted by means of screen-printed electrodes (SPE). In agreement with our previous study, the electrode mechanism at SPE is virtually identical as for GCE [47,81]. Aqueous solutions with concentrations from 1×10^{-4} to $7 \times 10^{-3} \text{ mol L}^{-1}$ were inserted into a sealed glass chamber with a volume of 1 L and left for 3 h to establish an equilibrium between the liquid and gas phases. 50 μL of the optimized solution of PAA and Cu^{2+} ions were added dropwise to the SPE and the electrode was inserted in the glass chamber. PAA has a gas-absorption capability providing the

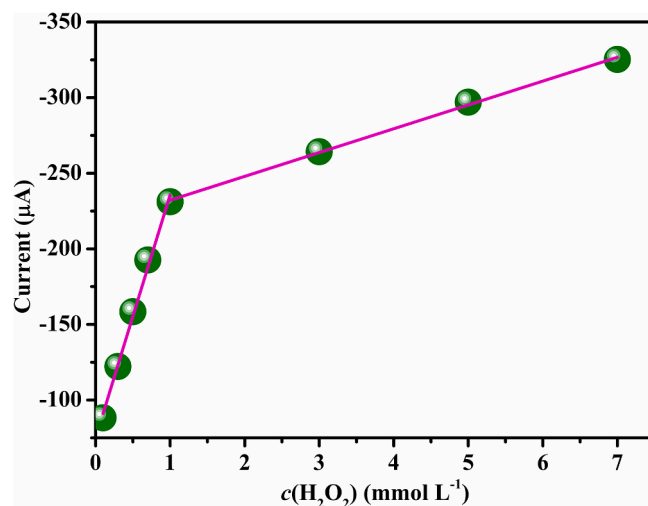


Fig. 8. Calibration curves created from measurements carried out for various concentrations of gaseous H_2O_2 in the chambers. Measurements were taken by square-wave voltammetry, 3 min after the SPE was inserted and sealed inside the glass chamber. The abscissa displays the concentrations of the aqueous H_2O_2 solutions inserted in the chamber to be equilibrated with the gas phase. The other conditions are the same as in Fig. 7.

Table 2

Comparison of LOD of different materials for gaseous H_2O_2 detection.

S. No	Material	Method	Reaction mode	LOD (mol L^{-1})	Ref.
1	Cu^{2+} mediator	SWV	Reduction	4.2×10^{-9}	[47]
2	PAA sensor MnO_2 PAA	CV	Oxidation	5.9×10^{-8} 8.8×10^{-8}	[8]
3	copper redox mediator	Amperometry	Oxidation	1.6×10^{-5}	[3]
4	Cu^{2+} mediator	SWV	Reduction	5.6×10^{-12}	This work

equilibrium at the liquid/gas interface to be established after 3 min. Afterwards, the electrochemical measurement was performed using SWV. The current was recorded at a potential of -0.750 V vs. Ag-quasi-reference electrode of the SPE, corresponding to -0.450 V vs. the conventional Ag/AgCl reference electrode. A linear dependence of the measured net current against the concentration of H_2O_2 was found over two concentration ranges, i.e., 1×10^{-4} – $1 \times 10^{-3} \text{ mol L}^{-1}$ and 1×10^{-3} – $7 \times 10^{-3} \text{ mol L}^{-1}$, considering the concentration of H_2O_2 in the solutions inserted into the glass chamber to saturate the gas phase with H_2O_2 over 3 h. Using the Henry law, the overall concentration interval in the gas phase is from 3.7×10^{-11} to $2.6 \times 10^{-9} \text{ mol L}^{-1}$ ($H^g = 1.1 \times 10^3 \text{ mol m}^{-3} \text{ Pa}^{-1}$ [55,56]). The correlation coefficients for the two concentration intervals are $R^2 = 0.9940$ and 0.9984 , respectively, as shown in Fig. 8. The repeatability of the measurement was calculated from 3 separate measurement series, with the standard deviation ranging from 0.29 % and 3.48 %. Based on the calibration curves considering aqueous H_2O_2 concentrations, LOD and LOQ values are $1.5 \times 10^{-5} \text{ mol L}^{-1}$ and $5.0 \times 10^{-5} \text{ mol L}^{-1}$, respectively. These values are calculated for the concentration range of 0.1 to 1 mmol/L (corresponding concentrations in the gas phase are 3.7×10^{-11} to $3.7 \times 10^{-10} \text{ mol L}^{-1}$; corresponding LOD and LOQ for the gas phase are 5.6×10^{-12} and 1.8×10^{-11}). A comparison of this work with other studies for gaseous H_2O_2 detection is provided in Table 2.

4. Conclusion

In continuation of our exploration into the intricate electrochemistry of hydrogen peroxide within polyacrylic acid while copper ions are present, this study focuses on the electrocatalytic process characterized by a robust reduction current tail at potentials more negative than -0.400 V (vs. to Ag/AgCl (3 mol L^{-1} KCl)), enabling exceptional detection sensitivity even at concentrations as low as $10^{-11} \text{ mol L}^{-1}$ of H_2O_2 in the gas phase. The underlying hypothesis suggests that the electrode mechanism follows a second-kind electrocatalytic reaction pathway [68]. Within the bulk of the aqueous polyacrylic solution, an inherent Fenton-like redox chemistry spontaneously unfolds between copper ions and H_2O_2 , resulting in the generation of reactive oxygen species (ROS). It is postulated that these ROS species undergo electrode reduction, subsequently rejuvenating H_2O_2 in the proximity of the electrode. This interplay establishes a self-regenerative electrocatalytic electrode mechanism. Notably, the intensity of this electrocatalytic process evidently hinges on the concentration of polyacrylic acid, underscoring its pivotal role in the comprehensive electrochemical process via the stabilizing influence exerted on both copper ions and ROS species.

In conjunction with square-wave voltammetry and other sophisticated technique variants, the study convincingly demonstrates the capability to detect minute concentrations of H_2O_2 gas. This achievement is made possible by utilizing readily available screen-printed electrodes, necessitating a mere 3-minute equilibration period between the gas phase and the modified screen-printed electrodes.

CRediT authorship contribution statement

Nabi Ullah: Writing – original draft, Methodology, Formal analysis, Investigation, Data curation, Writing – review & editing. **Dariusz Guziejewski:** Writing – review & editing, Resources, Project administration. **Bartłomiej Barton:** Validation, Formal analysis, Investigation, Data curation, Writing – review & editing. **Valentin Mirceski:** Conceptualization, Writing – review & editing, Supervision, Methodology, Validation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded in whole or in part by National Science Center, Poland 2020/39/1/ST4/01854. For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

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Detection of gaseous hydrogen peroxide using polyacrylic acid–copper(II) catalytic system at carbon-based screen-printed electrodes

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Received: 15 June 2025 / Revised: 4 August 2025 / Accepted: 24 August 2025 / Published online: 13 September 2025
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Abstract

This study concerns the electrochemical detection of hydrogen peroxide in the gas phase using screen-printed electrodes (SPEs). The research employs cyclic and square-wave voltammetry techniques to leverage equilibrium dynamics between the solution and gas phases for detecting gaseous analytes. A thorough study of the effect of the immobilized redox mediator on the complex redox environment, containing polyacrylic acid, copper ions, and hydrogen peroxide, is being analyzed. The detection system utilizes SPEs modified with Prussian blue and covered with a minute amount of supporting electrolyte, ensuring minimal cross-contamination and high sensitivity. The optimized methodology demonstrated a linear response to hydrogen peroxide concentrations within the gas phase, spanning a range approximately from the picomolar to nanomolar range. This low-concentration range validates the potential of the SPE platform for real-time monitoring of hydrogen peroxide, with implications for various industrial and biomedical applications. These findings contribute to advancing electrochemical sensing technologies for gas-phase analyte detection, setting the stage for further exploration in environmental monitoring and analytical chemistry.

Keywords Hydrogen peroxide detection · Electrochemical gas phase analysis · Screen-printed electrodes · Square-wave voltammetry · Electrochemical gas sensor · Volatile analyte monitoring

Introduction

Hydrogen peroxide is a naturally occurring biomolecule that has become indispensable in various facets of daily life, including the cosmetic, textile, paper, and biomedical industries, as well as in both inorganic and organic syntheses [1, 2]. Its wide-ranging utility extends to the pharmaceutical and food production sectors, owing to its potent bactericidal properties [3]. Furthermore, within the human body, hydrogen peroxide serves vital functions with profound chemical and biological significance [4]. In biochemistry, hydrogen peroxide is essential for oxidative biosynthesis reactions and has a defensive role against bacteria in physiological fluids such as urine and saliva [5, 6]. Additionally, it can function as a biomarker of oxidative stress [7], with elevated levels potentially indicating serious health conditions such as asthma and lung cancer [8, 9]. Early diagnosis facilitated by hydrogen peroxide detection could enable the treatment of many patients at an early stage of disease development.

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However, hydrogen peroxide's versatile chemistry has also made it a commonly chosen substance for the production of homemade explosives by terrorists [10, 11]. Peroxo-based explosives appeal to attackers due to the ease with which they can be prepared by combining commercially available precursors, including hydrogen peroxide, alcohol, and acetone [11]. However, detecting these unstable and sublimating explosives remains challenging due to the absence of nitro groups [12, 13].

Therefore, the detection of hydrogen peroxide in the gaseous phase is of particular importance. While standard methods such as chromatography or spectrometry exist, chromatographic determination is complex and costly, typically limited to specialized laboratories. Additionally, spectroscopy is hindered by the lack of absorption or emission characteristics of hydrogen peroxide in the visible and UV range [14]. Consequently, electrochemical methods have garnered significant interest in recent years due to their numerous advantages, including simplicity, short analysis time, robustness, potential for on-site detection, portability, and instrument miniaturization [15–19]. The increasing demand for in-situ research and equipment miniaturization is met by the well-established screen-printed technology and electrodes (SPEs) [20], specifically carbon-based SPEs (SPCEs) modified with various electrocatalysts [21–23], such as Prussian blue (PB) [24–26], cobalt(II) phthalocyanine (CoPC) [27], and others [28–30].

Recently, we have developed a system capable of adsorbing gaseous hydrogen peroxide and facilitating electrocatalytic detection at trace levels through the electrocatalysis of copper(II) ions [18, 19]. The current study aims to explore the capabilities of commercially available SPEs modified with (PB) and (CoPC) for gaseous hydrogen peroxide detection utilizing an aqueous solution of polyacrylic acid (PAA) in the presence of copper(II) ions as a catalyst. In this context, PAA was employed as part of the supporting electrolyte, primarily to provide a stable environment and facilitate the dissolution of gaseous hydrogen peroxide for stability in the aqueous phase. Its favorable properties, such as high water absorption, aqueous gel-forming ability, and compatibility with electrochemical systems, make it a practical medium for maintaining the gas–liquid interface required for efficient analyte transfer. While PAA does not participate directly in the electrocatalytic reaction, it plays an important background role in creating favorable conditions for reliable H₂O₂ detection. Consequently, our goal is to develop an optimal hydrogen peroxide detection system, leveraging both the electrocatalytic effect of copper(II) ions combined with PAA solution and the electron-mediating properties of the electrode surface modifiers.

Experimental

All chemicals used were of analytical grade and used as received from Sigma-Aldrich. All stock solutions of KNO₃ (0.1 mol L⁻¹), equimolar K₃[Fe(CN)₆] and K₄[Fe(CN)₆] (0.1 mol L⁻¹), CuSO₄ (0.1 mol L⁻¹), and H₂O₂ (0.1 mol L⁻¹, 0.01 mol L⁻¹, and 0.001 mol L⁻¹) were prepared using deionized water (DI water) obtained by the Polwater DL-3 purification system. To prepare a 1% (mass percentage) solution of PAA in 0.1 mol L⁻¹ aqueous solution of KNO₃, non-crosslinked PAA with a molecular weight of 450,000 g mol⁻¹ was used. The latter solution has a pH value of 2.9 and served as a supporting electrolyte.

The following types of screen-printed carbon-based electrodes were used (all from Metrohm-Dropsens, Spain): bare screen-printed carbon electrode (ref. 110), screen-printed Co-phthalocyanine/carbon electrode (ref. 410), and screen-printed Prussian blue/carbon electrode (ref. 710). Each electrode features an identical working electrode surface area of 0.1256 cm². Unless otherwise stated, measurements were carried out in the presence of oxygen at room temperature.

The study of hydrogen peroxide in the gas phase was conducted using a tightly sealed glass chamber with a volume of 1 L saturated with ambient air. Inside the chamber, 50 mL of an aqueous hydrogen peroxide solution with a concentration ranging from 0.1 to 10 mmol L⁻¹ was introduced and left to establish equilibrium between the Liquid and gas phases. After 3 h, determined as the necessary stabilization time, an SPE was introduced into the glass chamber. The active surface (the surfaces of the three electrodes) of the SPE had been pre-coated with 50 µL of an optimized solution containing 1% PAA in 0.1 mol L⁻¹ KNO₃, supplemented with copper(II) sulfate (0.2 mmol L⁻¹). The electrode with the applied solution remained inside the chamber for 3 min to enable the dissolution of gaseous hydrogen peroxide into the supporting electrolyte on the SPE.

All potentials were referred to a silver quasi-reference electrode. Electrochemical measurements using cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed with an Autolab PGSTAT 302N controlled by Nova (v. 2.1.5) software (Metrohm-Autolab, Netherlands).

Results and discussion

Electrochemical characterization with cyclic voltammetry

In the initial phase, the CV technique was employed to briefly characterize the fundamental properties of a bare

SPE using an equimolar system of hexacyanoferrate(II)/(III) in a solution of $0.1 \text{ mol L}^{-1} \text{ KNO}_3$. The electrode reaction exhibited typical, quasi-reversible character, in agreement with literature data [31]. Measurements conducted in the scan rate range from 0.02 to 0.5 V s^{-1} indicated a quasi-reversible, diffusion-affected electrode process [32]. Importantly, based on the Randles–Ševčík equation, the diffusion coefficients of both forms of the redox couple hexacyanoferrate(II)/(III) have been estimated in a supporting electrolyte containing 1% PAA and $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ (inset of Fig. 1). These values are 7.11×10^{-6} and $6.64 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for hexacyanoferrate(II) and hexacyanoferrate(III) ions, respectively. The calculated diffusion coefficients are in close proximity to the literature value reported by Niu et al. [33] for the aqueous electrolyte free of PAA, implying that the latter does not significantly affect the diffusion features of the redox species.

Typical cyclic voltammograms recorded at an unmodified carbon screen-printed electrode, in the supporting electrolyte containing 1% PAA and $0.1 \text{ mol L}^{-1} \text{ KNO}_3$, are presented in Fig. 1, comparing the effects of copper(II) ions (0.2 mmol

L^{-1}), used as a catalyst, and hydrogen peroxide (1 mmol L^{-1}) as an analyte. Upon addition of hydrogen peroxide in the absence of copper ions, a slight shift of the cathodic tail towards less negative values is noticeable (cf. curves a and b in Fig. 1), indicating a very sluggish electrode reduction of hydrogen peroxide. On the other hand, in the presence of the catalyst only, i.e., copper(II) ions, a distinct cathodic peak emerges at potentials of ca. -0.2 V , characteristic of the reduction of Cu^{2+} ions to Cu^+ and further to Cu(s) (curve c in Fig. 1) [19]. In parallel, there is an increase in the cathodic current at more negative potentials in the form of a current tail, suggesting facilitated oxygen reduction in the presence of copper(II) ions. This assumption is supported by the absence of such a current tail in the absence of oxygen (data not shown).

In the presence of both the catalyst (copper(II)) and hydrogen peroxide, the observed cathodic peak of copper ion reduction increases significantly and shifts slightly towards more positive potentials, which obviously confirms the electrocatalytic properties of copper ions via an EC' electrode mechanism (curve d), in accordance with our recent findings

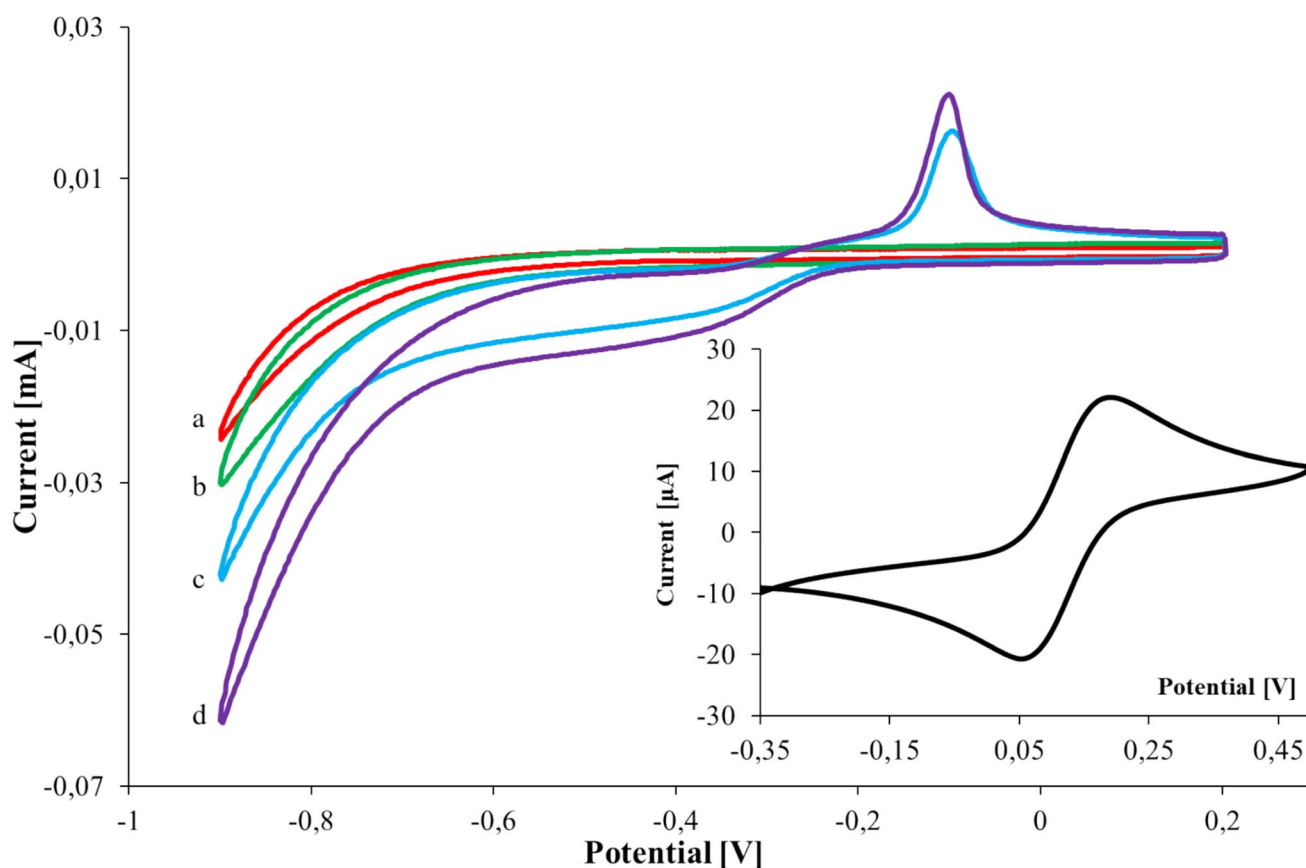


Fig. 1 Typical cyclic voltammograms recorded at a bare carbon screen-printed electrode at a scan rate of 50 mV s^{-1} in a supporting electrolyte consisting of 0.1 mol L^{-1} aqueous solution of KNO_3 and 1% (mass percentage) of PAA. Curve a is the blank response; b as

(a) with 1 mmol L^{-1} hydrogen peroxide; c as (a) with 0.2 mmol L^{-1} copper(II), and d as (a) with both copper ions and hydrogen peroxide. Inset: CV of 1 mM equimolar hexacyanoferrate(II)/(III) system recorded in the same supporting electrolyte at 50 mV s^{-1}

[18, 19]. Moreover, a significant increase in the cathodic tail is observed at more negative potentials, associated with the reductive catalytic process of hydrogen peroxide itself. It should also be noted that in the anodic potential region, an anodic stripping peak of the deposited elemental copper emerges at a potential ca. -0.1 V, that increases upon the addition of hydrogen peroxide as well, implying a complex redox interplay between copper species and the studied analyte.

To compare the properties of unmodified carbon screen-printed electrodes to those containing modifying redox mediators, an additional analysis has been performed by using cobalt(II) phthalocyanine (CoPC) and Prussian blue (PB) modified screen-printed electrodes. Figure 2 displays typical cyclic voltammograms recorded at CoPC-modified electrodes. The blank response in the same supporting electrolyte is associated with a cathodic peak located at a potential of -0.6 V, resulting from the irreversible oxygen reduction catalyzed by CoPC (Fig. 2, curve a) [34, 35]. It is noticeable that the CoPC modifying layer undergoes significant alterations upon potential cycling within a wide

potential window, resulting in a more intricate response (inset of Fig. 2). These changes entail, among others, the change of the cobalt oxidation state in the modifier structure, including the formation of reversible redox pairs $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ assigned to a formal potential of ca. -0.1 V, as well as irreversible transformations in the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ redox system, leading to the formation of Co^{I} at ca. -0.65 V (Fig. 2, inset) [35].

In the presence of hydrogen peroxide, the catalytic reductive peak of oxygen reduction is shifted toward more positive potentials (curve b in Fig. 2), implying interferences between the catalytic reduction of oxygen and hydrogen peroxide, both proceeding via complex adsorption-affected electrode reaction pathways [36–39]. In addition, in the presence of copper(II), the deposition of metallic copper takes place as implied by the anodic stripping peak at ca. -0.1 V (curve c in Fig. 2); yet the typical reductive peak of copper ions is overlapped with the strong catalytic response due to oxygen reduction at CoPC-modified electrode. This overlap may pose challenges for precise peak assignment and limit the analytical selectivity of the system. However, this limitation is partially offset by the distinct increase in cathodic

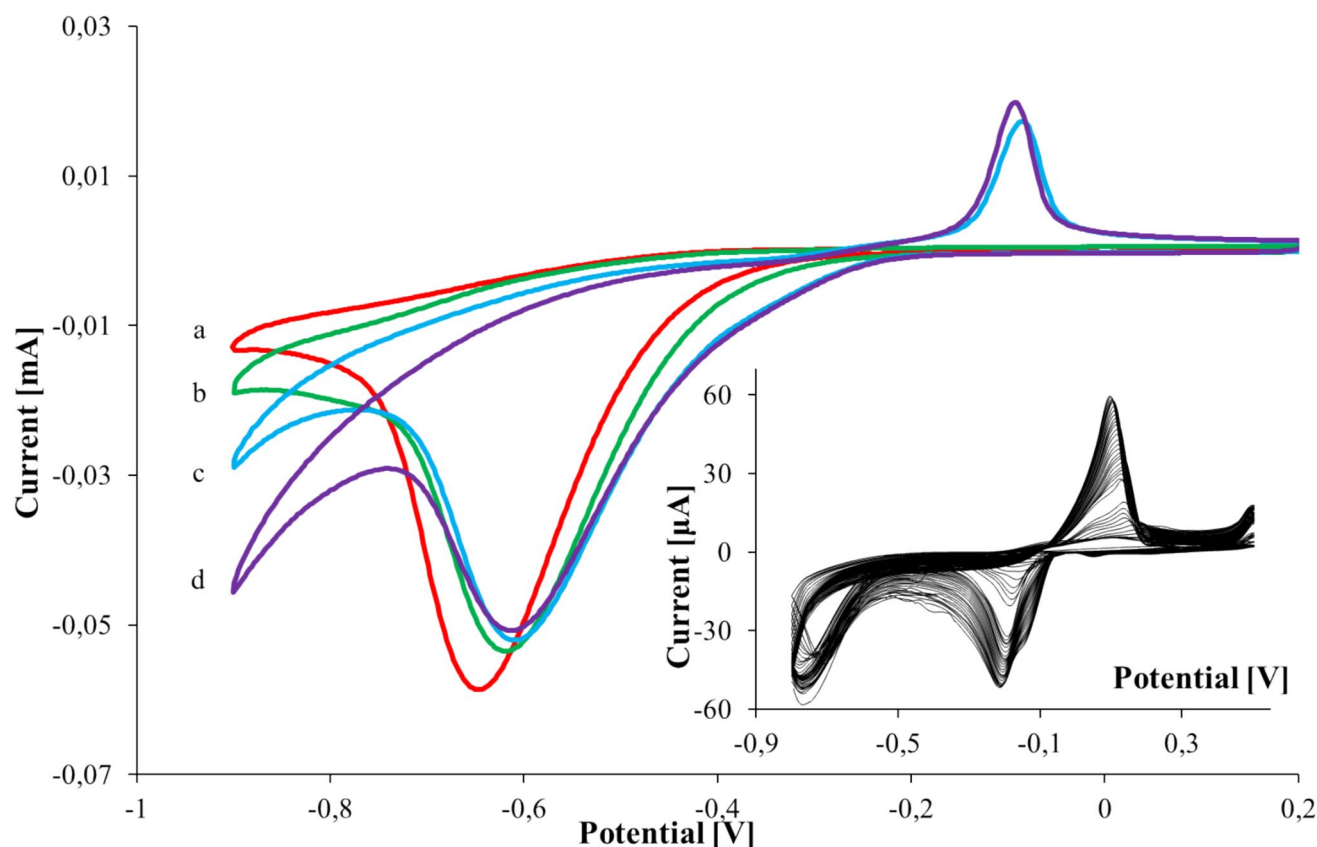


Fig. 2 Cyclic voltammograms recorded at a CoPC-modified screen-printed electrode at a scan rate of 50 mV s^{-1} in a supporting electrolyte consisting of 0.1 mol L^{-1} aqueous solution of KNO_3 and 1% (mass percentage) of PAA. Curve a is the blank response; b as (a) with 1 mmol L^{-1} hydrogen peroxide; c as (a) with 0.2 mmol L^{-1}

copper(II), and d as (a) with both copper ions and hydrogen peroxide. Inset: Repetitive CVs at the CoPC-modified carbon screen-printed electrode in the same supporting electrolyte within a broad potential window at 50 mV s^{-1}

current observed when both hydrogen peroxide and copper ions are present, which still enables consistent and reliable detection despite the overlapping signals. When both copper ions and hydrogen peroxide are present in the system (curve d in Fig. 2), the overall electrocatalytic response is enhanced, as implied by the pronounced increase in the reductive current commencing at about -0.2 V. In addition, the broad cathodic peak is shifted toward less negative potentials (ca. at -0.6 V), associated with the cathodic current tail at potentials more negative than -0.7 V, which is a general feature of any copper-hydrogen peroxide system [19].

Typical voltammograms of the PB-modified SPE in the studied supporting electrolyte are attributed to a pair of peaks typically observed for the quasi-reversible electrode reaction of the PB (curve a in Fig. 3) [40, 41]. Potential cycling over a wide potential range reveals the typical Prussian blue electrochemistry, involving the transformation of PB into Prussian white (PW) at about -0.1 V, and Prussian blue to Berlin green close to 0.4 V (Fig. 3, inset) [40, 41]. The presence of hydrogen peroxide causes a significant increase in the voltammetric response of the PB/PW redox

couple, yet the enhancement of the cathodic peak is more pronounced (Fig. 3, curve b), which is in agreement with literature findings [42]. Indeed, this behavior is closely related to the catalysis of hydrogen peroxide reduction by divalent iron ions [43]. In the presence of the catalyst copper(II) only, the response PB/PW electrochemical response also increases (Fig. 3 curve c), implying a complex redox interplay between the PB and copper(II) as well. However, in the presence of both copper ions and the analyte, a dramatic increase in the response is observed, as depicted by curve d in Fig. 3. Obviously, a synergistic effect is achieved by both the PB and the copper(II), providing a basis for highly sensitive determination of hydrogen peroxide.

It is well established that Prussian blue (PB) electrochemistry provides one of the most effective platforms for the electrochemical detection of hydrogen peroxide, based on the direct redox interaction between the iron(II)/iron(III) redox centers and hydrogen peroxide. Fundamentally, this process involves a heterogeneous redox reaction between solid-state Prussian blue, deposited on the electrode surface, and dissolved—and likely physisorbed—hydrogen peroxide.

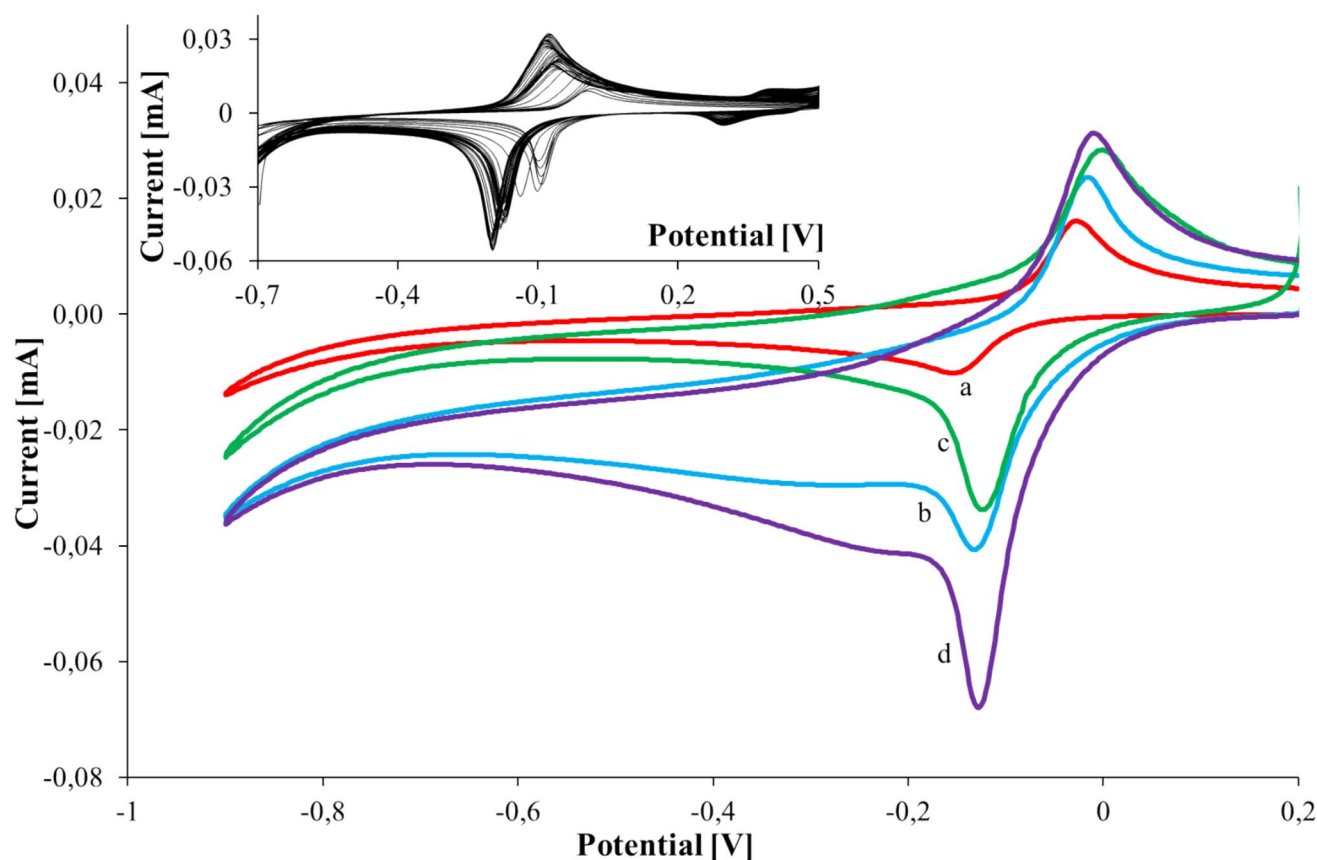
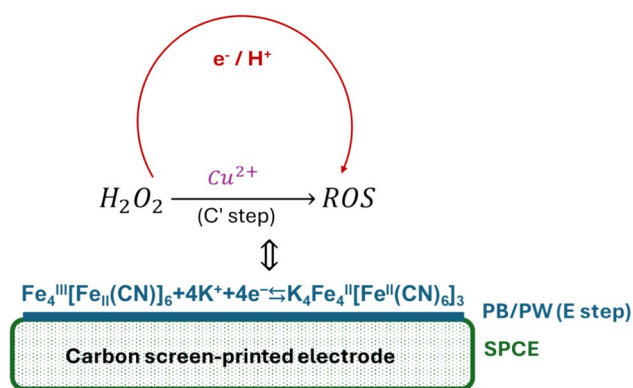


Fig. 3 CVs recorded at a PB-modified carbon screen-printed electrode at a scan rate of 50 mV s^{-1} in a supporting electrolyte consisting of 0.1 mol L^{-1} aqueous solution of KNO_3 and 1% (mass percentage) of PAA. Curve a is the blank response; b as (a) and 1 mmol L^{-1}

hydrogen peroxide; c as (a) and 0.2 mmol L^{-1} copper(II), and d as (a) with both copper ions and hydrogen peroxide. Inset: repetitive CVs at a PB-modified carbon screen-printed electrode in the same supporting electrolyte at 50 mV s^{-1}



Scheme 1 Schematic representation of the synergistic interplay of the electrode reactions in the developed electrochemical setup

As demonstrated in our previous studies [18, 19], in the presence of copper(II) ions, hydrogen peroxide undergoes spontaneous disproportionation, yielding a complex mixture of highly reactive intermediates (e.g., hydroxyl radicals, superoxide, etc.). In line with the experimental evidence obtained in the present study, we propose that these reactive intermediates exchange electrons with Prussian Blue at a higher rate than hydrogen peroxide itself, resulting in a synergistic catalytic effect between Prussian Blue and copper(II) ions. To further explain this complex interplay we have made an illustration given in Scheme 1.

Electrochemical characterization with square-wave voltammetry

In the advanced phase, square-wave voltammetry was employed to investigate further the features of the modified SPEs. Typical square-wave voltammograms comparing the effect of the catalyst, i.e., copper(II) ions (0.2 mmol L^{-1}) and the analyte hydrogen peroxide (1 mmol L^{-1}), in the supporting electrolyte (1% PAA in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$) on various screen-printed electrodes are presented in Fig. 4. For the bare-SPE (Fig. 4A), the addition of copper(II) in the absence of the analyte led to an increase in currents at highly negative potentials, indicating facilitated oxygen reduction (curve b). The additional introduction of hydrogen peroxide caused a slight shift of the net SW voltammogram toward less negative values, confirming our previous observations (curve c). In parallel, a significant increase in the net SW currents was observed in the potential region of the cathodic tail (i.e., more negative than -0.5 V), which is associated with the direct catalytic reduction of hydrogen peroxide. Additionally, peaks at potentials of -0.1 V and -0.4 V clearly indicate the stepwise reduction of Cu^{2+} to $Cu(s)$, which are both affected by hydrogen peroxide, following an EC' electrode reaction scheme as elaborated in [18].

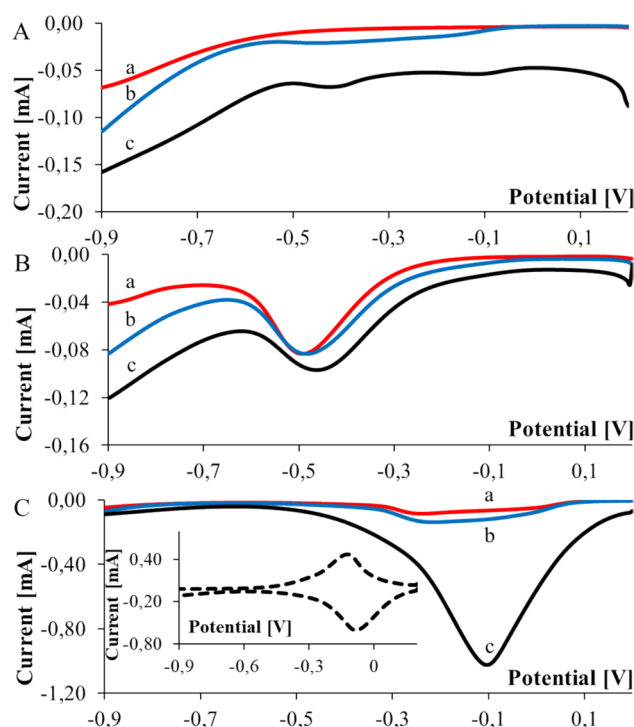


Fig. 4 Net SW voltammograms recorded at **A** bare carbon screen-printed electrode; **B** cobalt(II) phthalocyanine-modified screen-printed electrode; **C** Prussian blue-modified screen-printed electrode in a supporting electrolyte consisting of a 0.1 mol L^{-1} aqueous solution of KNO_3 and 1% (mass fraction) of PAA. The red curves a refer to the blank response; blue curves b are as (a) plus 0.2 mmol L^{-1} copper(II); black curves c are as (a) plus both copper ions and $1 \text{ mM H}_2\text{O}_2$. The inset of panel (C) shows forward and backward SW voltammetric components corresponding to the net voltammogram recorded in the presence of both copper ions and hydrogen peroxide (i.e., conditions for curve c). Parameters of the SW potential modulation are SW amplitude 0.2 V , SW frequency 8 Hz , and step potential -0.005 V

Figure 4B displays representative net SW voltammograms at CoPC-SPE. The SWV measurements performed for the blank sample in the supporting electrolyte only reveal a pronounced peak at -0.5 V (100 mV less negative than observed in CV), attributed to the irreversible oxygen reduction catalyzed by cobalt(II) phthalocyanine (Fig. 4B, curve a). In the presence of copper ions, a slight increase in the net currents is observed, due to additional reduction of copper(II) ions at -0.1 V (curve b). Enhanced oxygen reduction is also evident, as demonstrated by a significant increase in the cathodic tail and its shift toward less negative potentials.

The introduction of hydrogen peroxide into the system amplifies the recorded signals across the entire potential range, while slightly shifting the main voltammetric peak toward less negative potentials (curve c in Fig. 4B). The voltammetric peak is significantly broadened, reflecting a range of complex underlying phenomena, including

oxygen reduction catalyzed by both copper(II) ions and the cobalt(II) phthalocyanine layer, as well as the redox interactions between H_2O_2 and the two catalysts. Importantly, the reduction current at more negative potentials than -0.6 V, i.e., in the potential region of direct catalytic reduction of H_2O_2 , is significantly enhanced.

The application of SWV to the blank sample containing the supporting electrolyte at the Prussian blue-modified SPEs revealed a broad cathodic signal associated with the electrode reactions of the modifier, as shown in Fig. 4C (curve a). The introduction of copper ions significantly enhances the voltammetric response at approximately -0.1 V, implying complex redox interactions between different forms of Prussian blue and copper ions (curve b). The simultaneous presence of both copper ions and the analyte hydrogen peroxide dramatically increases the response (curve c). The voltammetric currents are up to an order of magnitude higher, confirming the synergistic effect between copper(II) and the PB modifier in the determination of hydrogen peroxide.

The square-wave voltammetry technique was employed to delineate the relationships between the recorded current at different electrodes and hydrogen peroxide concentration

ranging from 0.1 to 10 mmol L^{-1} in the presence of 0.2 mmol L^{-1} copper(II). For consistent comparison, the current was sampled at a potential of -0.75 V for each electrode type, i.e., in the potential region corresponding to the direct electrode reduction of hydrogen peroxide. The resulting calibration curves, derived from three independent measurement series, are presented in Fig. 5. All three SPEs exhibited the same linear dependence, though with varying slopes, and over two concentration ranges, namely 0.1 to 1 mmol L^{-1} and 1 to 9 mmol L^{-1} . Here, a deviation was noted in the case of the modified SPEs, as the linear dependence of CoPC-SPE ended at a concentration of 7 mmol L^{-1} (curve b), whereas PB-SPE exhibited linear dependence only up to 6 mmol L^{-1} .

When comparing the calibration curves obtained for all SPEs corresponding to the direct reduction of H_2O_2 , the bare SPEs exhibited the best analytical performance, demonstrating higher sensitivity (curve a). Additionally, the recorded currents were the highest among the tested electrodes. The collected calibration curves suggest that under the studied conditions, the most optimal system for determining hydrogen peroxide in the liquid phase is the unmodified SPE with the addition of the electrocatalyst in the form of

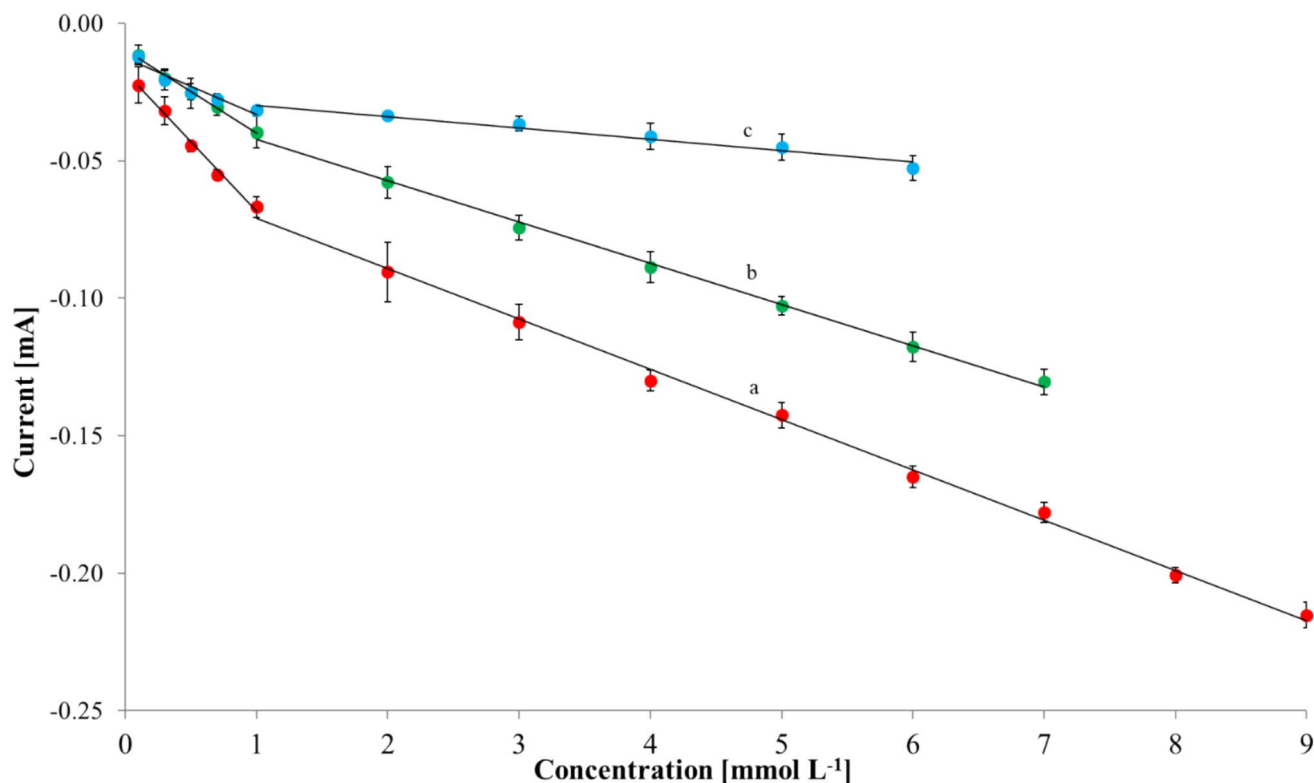


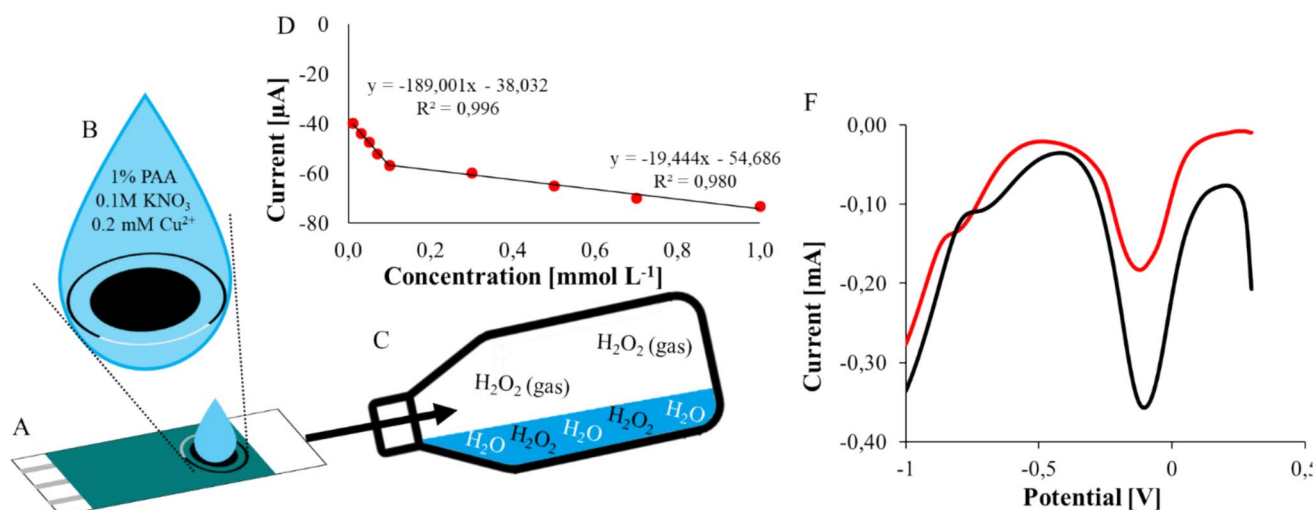
Fig. 5 Calibration curves for the quantification of hydrogen peroxide (0.1 – 9 mM) in a liquid phase obtained on a bare carbon screen-printed electrode (red curve a), CoPC-modified screen-printed electrode (green curve b), and PB-modified screen-printed electrode (blue

curve c) in a supporting electrolyte consisting of a 0.1 mol L^{-1} aqueous solution of KNO_3 and 1% (mass fraction) of PAA, containing 0.2 mmol L^{-1} copper(II) ions. The SW parameters are as in Fig. 4

copper(II) ions. Clearly, this conclusion holds when we take into account the direct, catalyzed electrochemical reduction of hydrogen peroxide at a relatively negative potential of -0.75 V.

The observed relationship between Prussian blue and hydrogen peroxide in the presence of copper(II) ions laid the foundation for an indirect method of analyte determination, where both Prussian blue and copper ions synergistically shuttle electrons between the electrode

and hydrogen peroxide. Scheme 2 depicts the calibration curves constructed from five series, measuring the intensity of the main net SW voltammetric peak at a potential of -0.1 V (cf. Figure 4C) within the concentration range of hydrogen peroxide dissolved in the supporting electrolyte from 0.01 to 1 mmol L $^{-1}$. The use of electrochemical reduction of Prussian blue, with the additional catalytic effect of copper(II) ions, significantly lowered the detection limit to the micromolar level for the determination of



Scheme 2 Diagram of the measurement system for hydrogen peroxide detection in the gas phase. **A** Screen-printed electrode featuring three electrodes: a carbon working electrode, a silver quasi-reference electrode, and a carbon counter electrode, onto which 50 µL of supporting electrolyte containing 1% PAA in 0.1 M KNO₃ and 0.2 mmol L $^{-1}$ copper(II) is applied. **B** Close-up view of the working area of the system (the applied solution covers the surfaces of all three electrodes). **C** A tightly sealed glass chamber containing 50 mL of an aqueous solution with a specified concentration of hydrogen peroxide.

After 3 h of stabilization, the electrode with the applied solution is introduced into the chamber. **D** Current response as a function of hydrogen peroxide concentration dissolved in the supporting electrolyte (1×10^{-5} – 1×10^{-3} mol L $^{-1}$) recorded on the screen-printed electrode modified with Prussian blue, $n=5$. **E** Exemplary recorded response in the chamber: blank (red curve) and with 1 mM hydrogen peroxide (black curve). Parameters of the SW potential modulation are amplitude 0.05 V, frequency 8 Hz, and step potential -0.005 V

Table 1 Comparison of detection and quantification limits with data from the literature

Sensor	Method	LOD (mol L $^{-1}$)	Linear range (mol L $^{-1}$)	Matrix	Ref
SPE	Amperometry	1.6×10^{-8}	2.94×10^{-7} – 2.94×10^{-6}	Gas	[17]
GCE	SWV	1.17×10^{-4}	1×10^{-4} – 1×10^{-3} 1×10^{-3} – 7×10^{-3}	Gas	[19]
PB-GCE	Amperometry	3.0×10^{-7}	5.0×10^{-7} – 1×10^{-3}	Liquid	[44]
PBNCs/rGO-GCE	Amperometry	4.5×10^{-8}	5×10^{-8} – 1.2×10^{-4}	Liquid	[45]
PB-SPE	Amperometry	4.0×10^{-7}	4.0×10^{-7} – 1.0×10^{-4}	Liquid	[46]
PEI/Rh-NP-SPE	Amperometry	2.0×10^{-6}	5.0×10^{-6} – 6.0×10^{-4}	Liquid	[47]
Hb-Au-SPE	Amperometry	5.5×10^{-6}	—	Liquid	[48]
AgNP@GMR/SPE	Amperometry	2.0×10^{-5}	5.0×10^{-5} – 1.8×10^{-3} 1.8×10^{-3} – 5×10^{-3}	Liquid	[49]
PBNPs-SPE	Amperometry	2.0×10^{-5}	2.0×10^{-5} – 7.0×10^{-4}	Liquid	[50]
Ti ₃ C ₂ T _x MXene/FCN-SPCE	CV	1.18×10^{-10}	1.47×10^{-8} – 8.82×10^{-7}	Gas	[51]
PAA-SPE	CV	5.9×10^{-8}	4.41×10^{-7} – 3.56×10^{-6}	Gas	[2]
PB-SPE	SWV	2.3×10^{-6}	1×10^{-5} – 1×10^{-3}	Liquid	This work

PBNCs Prussian blue nanocubes, rGO reduced graphene oxide, PEI polyethyleneimine, Rh-NP rhodium nanoparticles, Hb hemoglobin, AgNP silver nanoparticles, GMR graphene nanoribbons

hydrogen peroxide (comparison with our previous findings is given in Table 1).

The limit of detection (LOD) and quantification (LOQ) for the indirect sensing of hydrogen peroxide dissolved in the supporting electrolyte were calculated based on six averaged measurement series using standard formulas: $\text{LOD} = 3 \times S_d/b$, and $\text{LOQ} = 10 \times S_d/b$, where S_d is the standard deviation of the intercept and b is the slope of the calibration Line. The LOD was found to be $2.3 \times 10^{-6} \text{ mol L}^{-1}$, while the LOQ was $7.8 \times 10^{-6} \text{ mol L}^{-1}$. Notably, the relative standard deviation (RSD) for the five-measurement series was determined to be 1.4%, with a maximum value not exceeding 2.1%, indicating the high precision of the method. Recovery tests for hydrogen peroxide were also conducted, yielding results within the range of 90.4 to 110.3% across the entire concentration interval studied.

The final stage of the research focused on detecting hydrogen peroxide in the gas phase. Briefly, a dark glass bottle containing the ambient laboratory atmosphere was exposed to hydrogen peroxide solution with a volume of 50 mL, with a concentration ranging from 0.01 to 5 mmol L^{-1} . In our previous study [19], we performed time-course experiments with equilibration times ranging from 30 to 300 min. An equilibration period of 180 min consistently provided the most favorable balance between signal quality and experimental practicality. Based on those findings, the same duration was adopted in the present work. Afterwards, the electrochemical recording procedure began, where a screen-printed electrode, covered with 50 μL of the supporting electrolyte solution and connected via a cable connector, was introduced into the bottleneck and the entrance was sealed tightly. Following a 3-min preconditioning period, square-wave voltammetry was performed over a potential range of 0.2 to -0.9 V , with the measurement requiring 14 s to complete. The experimental procedure closely followed the methodology described in our previous work [19]. We demonstrated that the supporting electrolyte, with its remarkably enhanced redissolution of gaseous hydrogen peroxide in a polyacrylic acid-containing solution, facilitates electrochemical processes driven by the synergistic catalysis of Prussian blue (PB) and copper ions. This system provides a viable basis for the detection and quantification of hydrogen peroxide in the gaseous phase. Our experiments confirmed a linear response of the system to hydrogen peroxide concentrations, effectively covering a gas-phase concentration range approximately from 4 pmol L^{-1} to 2 nmol L^{-1} , which was calculated considering concentrations of hydrogen peroxide in aqueous solutions used for saturation of the gas phase and Henry's law [52, 53]. The estimated gas concentrations may vary slightly due to the degradation of hydrogen peroxide in the solution used to saturate the gas phase [54]; however, this effect is considered negligible within the concentration range used.

In contrast to our previous work [19], where the combination of polyacrylic acid and copper(II) ions was applied to facilitate the reduction of hydrogen peroxide, the present study offers several key advancements. One of the most significant is the introduction of Prussian blue as a co-catalyst, resulting in a synergistic enhancement of the electrochemical response, which was not exploited in the earlier approach. This dual-catalyst system not only lowers the detection limit by approximately one order of magnitude but also improves the linearity and reproducibility of the measurements. In addition, the sensing protocol has been carefully refined: square-wave voltammetry was optimized for fast and reliable detection, and screen-printed electrodes were adapted specifically for efficient measurements in the gas phase. Altogether, these improvements represent a shift from an initial proof-of-concept toward a more robust and practically applicable platform for gas-phase hydrogen peroxide sensing.

While the indirect estimation of vapor-phase H_2O_2 using Henry's law allows for approximate quantification, this approach carries important assumptions and limitations. It presumes complete gas–liquid equilibrium and does not account for possible degradation of H_2O_2 in the aqueous or gas phase due to light, temperature, or catalytic surfaces. Control experiments with PAA-only solutions did not elicit significant electrochemical responses. Despite these limitations, the voltammetric signal scaled linearly with the expected gas-phase concentrations, suggesting the method offers a valid semi-quantitative approximation. Future validation would further confirm the accuracy of the presented estimation.

Conclusions

In this work, we have presented the overall behavior of SPEs and their CoPC and PB modifications for sensing hydrogen peroxide. The experimental conditions incorporated polyacrylic acid as a medium to enhance the redissolution of the analyte from the gaseous phase, alongside copper ions as an efficient electrocatalyst. We characterized the studied system using both cyclic and square-wave voltammetry, demonstrating that the use of polyacrylic acid does not negatively impact the electrochemistry of the investigated redox couples.

A notable synergistic effect was observed between copper ions and hexacyanoferrate, highlighting the advantages of using coupled electrocatalysts. Although the system exhibits considerable complexity regarding mechanistic analysis, its analytical utility offers significant improvements, underscoring its potential for practical sensing applications. Most of all, this work successfully demonstrates the application of a modified screen-printed electrode system for detecting

hydrogen peroxide in the gas phase, utilizing a robust electrochemical protocol based on square-wave voltammetry. By achieving a linear response over a gas-phase concentration range approximately from 4 pmol L⁻¹ to 2 nmol L⁻¹, the study underscores the reliability and precision of the proposed methodology.

The results of this study highlight the potential of electrochemical sensors to bridge gaps in real-time monitoring technologies, reinforcing their role in advancing analytical and environmental chemistry. This study serves as a significant step toward practical and efficient electrochemical sensing platforms, with broad implications for environmental monitoring, industrial safety, and healthcare diagnostics.

Acknowledgements This research was funded in whole or in part by National Science Center, Poland 2020/39/I/ST4/01854. For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

Author contributions Conceptualization DG, VM; Data curation BB; Formal analysis BB; Funding acquisition VM; Investigation BB, NU, DG; Methodology DG, VM; Project administration DG; Supervision DG, VM; Validation DG; Visualization BB, NU; Writing—original draft BB, DG, VM; Writing—review & editing PK, NU, VJ, DG, VM.

Funding This research was funded in whole or in part by the National Science Center, Poland 2020/39/I/ST4/01854. For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

Data availability Data available upon request from corresponding author.

Declarations

Ethics approval Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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RESEARCH ARTICLE

Polyelectrolyte-Enhanced Electrochemical Sensing of Gaseous Hydrogen Peroxide With Copper(II)–Mediating Systems

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Received: 30 September 2025 | **Revised:** 6 January 2026 | **Accepted:** 13 January 2026

Keywords: electrochemical gas-phase analysis | H₂O₂ detection | screen-printed electrode | square-wave voltammetry | volatile analyte monitoring | voltammetric gas sensor

ABSTRACT

Hydrogen peroxide (H₂O₂) plays a crucial role in both biological and industrial applications; hence, there is a growing need to develop methods that enable reliable and efficient detection. While traditional techniques such as spectrophotometry and fluorescence provide high sensitivity, electrochemical methods offer rapid, cost-effective, and real-time monitoring capabilities. This study explores the role of polyelectrolytes as supporting electrolytes in enhancing electrochemical detection of hydrogen peroxide using copper(II)-mediated electrocatalysis. Building upon our previous research utilizing polyacrylic acid (PAA), alternative polyelectrolytes, including poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (pAMPS) and poly(acrylamide-co-acrylic acid) (pAAmAA), were investigated. Cyclic and square-wave voltammetry were employed to assess the impact of these polymers on the electrochemical performance. Results indicated that pAMPS strongly complexed Cu²⁺, reducing catalytic efficiency, whereas neutralized pAMPS improved Cu²⁺ availability, enhancing H₂O₂ reduction. Among all tested electrolytes, 1% pAAmAA demonstrated the highest sensitivity for direct H₂O₂ reduction and was subsequently selected for the gas-phase studies. Further optimization involved modifying pAMPS' pH, revealing that pAMPS at pH 2 significantly enhanced overall catalytic activity. The combination of pAMPS and pAAmAA with Prussian blue-modified screen-printed electrodes enabled H₂O₂ gas-phase detection down to 1.8×10^{-10} mol L⁻¹. These findings highlight the potential of polyelectrolyte-based electrolytes for improving the sensitivity and selectivity of electrochemical hydrogen peroxide detection, particularly in gas-phase applications.

1 | Introduction

The accurate detection of hydrogen peroxide (H₂O₂) remains a subject of great interest due to its significant role in both biological processes and industrial applications. H₂O₂ is widely used in pharmaceuticals, food production, cosmetics, and biomedical science [1, 2]. Beyond these applications, its significance in living organisms is particularly critical, as it plays a key role in various physiological processes [3]. In the human body, H₂O₂

participates in molecular signal transmission, regulation of cell proliferation, and immune responses against pathogens [4, 5]. Importantly, it also serves as a key biomarker of oxidative stress, reflecting the redox state and homeostatic balance within cells and tissues [4, 6]. Excessive levels or dysregulated production of hydrogen peroxide can lead to oxidative imbalances, contributing to chronic diseases such as neurodegenerative disorders, cardiovascular conditions, and cancer [6–8].

Various methods have been developed for H_2O_2 detection, with spectrophotometry [9–11], chemiluminescence [12, 13], and fluorescence [14] being among the most common ones. While these techniques offer high precision and reliability, they often require expensive instrumentation, skilled personnel, and complex sample preparation and are seldom applicable for real-time monitoring [15]. Electrochemical sensors, on the other hand, provide a rapid, cost-effective, and direct alternative for H_2O_2 detection under actual conditions.

A key factor in electrochemical analysis is the choice of a supporting electrolyte, which influences ionic conductivity, electrochemical efficiency, reaction kinetics, selectivity, and chemical stability [16–18]. Besides ensuring adequate ionic conductivity, the supporting electrolyte plays a fundamental role in establishing chemical equilibria necessary for analyte mobility, stability and reactivity. Additionally, it affects the rate and efficiency of the electron transfer at the electrode surface, thus directly impacting electrode kinetics and overall sensor performance [19]. Our previous studies [20–23] explored polyacrylic acid (PAA) as a supporting electrolyte due to its excellent polyelectrolyte properties, high water retention properties, biocompatibility, and ability to form thin semisolid layers. Although effective in detecting hydrogen peroxide, PAA proved inadequate for measurements below a specific concentration threshold. To overcome these limitations, we sought alternative stable polyelectrolytes. Based on literature data, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (pAMPS) and poly(acrylamide-co-acrylic acid) (pAAmAA) were selected for evaluation [24–30].

Specifically, pAMPS is a nontoxic, amphiphilic polymer with high chemical stability and conductivity, attributed to its functional groups [24–27]. It exhibits strong water absorption and is highly soluble in both water and dimethylformamide [28]. pAAmAA, containing both amide and carboxylic groups, offers good water solubility and superabsorbent properties [29, 30] due to strong H-bond formation. The choice of PAA, pAMPS, and pAAmAA was motivated by their distinct chemical functionalities and known differences in Cu^{2+} interaction strength, which make them suitable model systems for comparative evaluation. PAA was selected as a commonly used carboxylate-containing polymer with relatively moderate metal-ion binding, while pAMPS represents a polymer with strong Cu^{2+} complexation due to its sulfonate groups. pAAmAA was included as a mixed-functionality material to provide an intermediate reference between these two extremes. Evaluating these polymers in parallel enabled a direct comparison of how polymer composition influences electrochemical response and practical performance, thereby strengthening the overall assessment of the system.

This study evaluates and compares selected functional polymers and copolymers as a backbone of supporting aqueous electrolytes for hydrogen peroxide detection in the presence of copper(II) ions as an electrocatalyst. The optimization focuses on enhancing conductivity, stability, and sensitivity to improve performance and reliability in real-time gas-phase H_2O_2 sensing applications. In contrast to our previous studies, which focused exclusively on PAA-based systems, the present work introduces a systematic comparison of three structurally distinct polyelectrolytes, enabling us to identify how their different Cu^{2+} interactions affect both the direct and mediated electrochemical reduction of H_2O_2 . This broader experimental framework provides the basis

for selecting conditions under which alternative polymers outperform PAA in aqueous and gas-phase H_2O_2 detection.

2 | Experimental

All reagents used in this study were of analytical grade and applied as received from Merck and ThermoFisher. Stock solutions of KNO_3 (0.1 mol L^{-1}), CuSO_4 (0.1 mol L^{-1}), NaOH (0.5 mol L^{-1}), and H_2O_2 (0.1 mol L^{-1} , 0.01 mol L^{-1}) were prepared using deionized water obtained from a Polwater DL-3 purification system. Aqueous solutions of the polymer or copolymer at 1% (mass percent) were prepared by dissolving 1 g of polymer in 0.1 mol L^{-1} KNO_3 solution. For other concentrations, the required amount of polymer was adjusted accordingly, while maintaining the same concentration of KNO_3 solution. Polymer solutions were prepared using pAMPS with an average molecular weight of $\approx 2\,000\,000 \text{ g mol}^{-1}$, pAAmAA with an average molecular weight of $\approx 520\,000 \text{ g mol}^{-1}$, and noncrosslinked PAA with a molecular weight of about $450\,000 \text{ g mol}^{-1}$, respectively.

To conduct gas-phase experiments, commercially available screen-printed electrodes (SPEs) from Metrohm–Dropsens (Spain) were employed, specifically bare screen-printed carbon electrodes (ref. 110) and Prussian blue (PB)-modified screen-printed carbon electrodes (ref. 710), which were used as received. All electrodes had an active surface area of 0.1256 cm^2 , while the PB film thickness was reported to be 0.05 cm by the manufacturer. In this part of the study, a 50 mL aqueous hydrogen peroxide solution of a defined concentration was introduced into a sealed 1 L dark glass chamber and left for 3 h to establish equilibrium between the liquid and gas phases. This equilibration process enabled the generation of a gaseous hydrogen peroxide concentration at a level calculated according to Henry's law [31, 32]. After stabilization, $50 \mu\text{L}$ of the selected supporting electrolyte solution containing Cu^{2+} ions was drop-cast onto the active surface of the SPE. The device, now coated with a thin polyelectrolyte film containing electrocatalytic copper ions but no hydrogen peroxide, was placed inside the chamber, allowing gaseous hydrogen peroxide to partition into the electrolyte film. The presence of polyelectrolytes facilitated repartitioning into the aqueous phase, and electrochemical measurements were performed in the fourth minute after SPE insertion into the chamber. A three-electrode system was used for electrochemical characterization in solution, consisting of a glassy carbon working electrode, an Ag/AgCl (3 mol L^{-1} KCl) reference electrode, and a platinum wire as the auxiliary electrode. Unless otherwise stated, all measurements were conducted at room temperature under oxygenated conditions.

Electrochemical measurements, including cyclic voltammetry and square-wave voltammetry, were conducted using an Autolab PGSTAT 302N potentiostat controlled by Nova software (v. 2.1.5, Metrohm–Autolab, Netherlands). In the standard three-electrode setup in solution studies, potentials were referenced to the Ag/AgCl electrode. For gas-phase measurements with SPEs, potentials were referenced to the integrated silver quasireference electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed over the frequency range of 0.1 Hz to $1 \times 10^6 \text{ Hz}$, with an AC amplitude of 5 mV , at the potential of 0.06 V without an external redox probe.

3 | Results and Discussion

To determine the optimal supporting electrolyte for hydrogen peroxide detection in the presence of copper(II) ions as a catalyst, cyclic voltammetry was utilized in the initial phase of the study. The CV experiments were conducted using all selected polymers under identical conditions: PAA, pAAmAA, and two forms of pAMPS—the native acidic form and the neutralized form with pH 7. Each polyelectrolyte was dissolved in 0.1 mol L^{-1} aqueous KNO_3 solution, which also served as a reference for comparison. In addition, all solutions contained $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ and $1 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$. Initial measurements were conducted using a conventional three-electrode system with a GCE serving as the working electrode. The results are presented in Figure 1.

The analysis of hydrogen peroxide is based on two distinct electrode processes: the direct reduction of H_2O_2 , with current sampled at potentials around -0.45 V , and indirectly, via reduction of Cu^{2+} ions occurring slightly below 0 V potential. These two mechanisms are interrelated, as copper ions serve as electrocatalysts in the direct reduction of hydrogen peroxide through the disproportionation mechanism [18], while the presence of hydrogen peroxide, in turn, enhances the reduction signal of Cu^{2+} through the regenerative electrocatalytic EC' mechanism [20, 21]. This mechanistic interdependence was further validated by kinetic analysis, where a clear reduction of Tafel slopes was observed in the presence of Cu^{2+} , confirming that the catalytic pathway facilitates faster electron transfer compared to the direct reduction pathway alone (Figure S1). Therefore, the work explores two complementary detection strategies: one based on monitoring the current resulting directly from hydrogen peroxide reduction, and the other relying on changes in the voltammetric signal of copper ions. This dual approach was consistently applied to assess and compare the analytical performance of the tested polyelectrolytes.

In addition to CV, SW voltammetric protocol was applied, which interrogates electrode processes at significantly distinct time scales in comparison to CV. As the presented study relies on a sophisticated combination of the electrolyte with homogeneously distributed copper ions as an electrocatalyst, and on signal performance screening via two distinct electrode mechanisms, it has therefore been decided to control the effectiveness of the

protocols with two techniques being strongly yet differently affected by the instrumental parameters. In most cases, the results were consistent, but within a few entries, the outcome was a technique- or parameter-dependent result. The overall electrochemistry is highly complex as it depends on the ability of particular polyelectrolyte to complex copper ions (thus on the amount of free copper ions), on the disproportionation rate of hydrogen peroxide driven mainly by free copper ions [18], on the rate of the homogeneous reaction between electrochemically generated copper(I) and hydrogen peroxide [19], on the stability and morphology of elemental copper deposited on the electrode surface as a product of the complete reduction of copper ions, on the viscosity of the solution determined by the content of the polymer that controls the rate of diffusional mass transfer of electroactive species, on the interaction of the polymer with the hydrogen peroxide via hydrogen bonding [27, 28], etc.

To further elucidate the interrelation of copper ions and PB as electrocatalytic agents, the impedance spectra recorded in the blank supporting electrolyte were fitted using a two-time-constant equivalent circuit that accounts for the carbon/PB interface, the intrinsic redox activity of the PB film, and ion diffusion within the PB lattice. The high-frequency response is associated with electronic coupling between the carbon substrate and the PB layer, whereas the mid-frequency semicircle corresponds to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox transitions within PB. The low-frequency linear region is attributed to finite-length diffusion of charge-compensating ions inside the PB film. Although two time constants can be distinguished, the mid-frequency semicircle partially overlaps with the diffusion-controlled region, indicating strong coupling between charge-transfer kinetics and ion transport within the PB layer. Upon addition of Cu^{2+} ions to the supporting electrolyte (cf. curves a and b in Figure S2), a clear change in the semicircle region is observed, reflected by a decrease in the charge-transfer resistance. This behavior provides direct evidence of a synergistic effect on the electron-transfer kinetics of the adsorbed PB layer, rather than the appearance of a mixed signal involving Cu^{2+} reduction. In the presence of Cu^{2+} ions, the slight reduction of the mid-frequency semicircle indicates a decrease in the effective charge-transfer resistance within the PB film. This effect is attributed to enhanced electron and ion transport resulting from Cu^{2+} interactions with the PB/polymer matrix, which

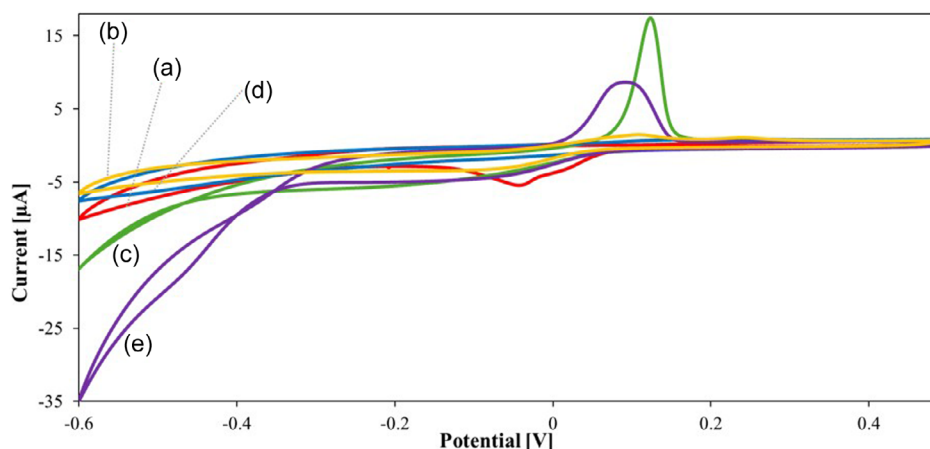


FIGURE 1 | Cyclic voltammograms recorded at a GCE, scan rate 50 mV s^{-1} in selected supporting electrolytes: (a) $0.1 \text{ mol L}^{-1} \text{ KNO}_3$, (b) pAAmAA, (c) PAA, (d) pAMPS, and (e) neutralized pAMPS (pH 7). Each polyelectrolyte was 1% (w/v), all studied solutions were prepared in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ with 1 mM hydrogen peroxide and $2 \times 10^{-4} \text{ mol L}^{-1}$ copper ions(II).

facilitate more efficient charge compensation during PB redox transitions. The limited magnitude of this change suggests that Cu^{2+} acts primarily as a kinetic promoter rather than introducing a new dominant charge-transfer pathway.

Additionally, a comparative analysis of the electrochemical response in the absence and presence of Cu^{2+} ions, both without and with increasing concentrations of hydrogen peroxide, is provided in Figure S3. These results clearly demonstrate that the combined system—comprising an adsorbed PB layer and solution-resident Cu^{2+} species—offers a highly effective platform for hydrogen peroxide electroanalysis. The analytical response is governed by the electrochemistry of PB, while the presence of Cu^{2+} ions significantly enhances the overall electrocatalytic performance.

3.1 | pAAmAA

As a reference for evaluating the performance of the tested polyelectrolytes, hydrogen peroxide reduction was first examined in the supporting electrolyte consisting of 0.1 mol L^{-1} aqueous KNO_3 solution without any polymer additive. In this system, a well-defined copper(II) reduction peak appeared at c.a. -0.1 V, providing the highest signal intensity among all recorded voltammograms (Figure 1, curve a). However, the cathodic current at more negative potentials—corresponding to the direct reduction of hydrogen peroxide—was relatively weak, indicating limited electrocatalytic activity in this electrolyte.

Utilizing the pAAmAA copolymer yielded a modest voltammetric response associated with Cu^{2+} reduction at about -0.1 V, and the cathodic tail related to direct hydrogen peroxide reduction also remained minimal (Figure 1, curve b). Actually, among the tested polymers, pAAmAA demonstrated only a limited enhancement of the voltammetric response of copper ions - compared to the considerably stronger response observed for PAA (Figure 1, curve c). Similarly, the cathodic current tail at potentials more negative than -0.4 V in the PAA solution was noticeably higher than that observed with pAAmAA.

The overall voltammetric behavior was further comparatively studied with square-wave voltammetry (Figure 2). The reference

voltammogram recorded in 0.1 M KNO_3 solution in the absence of a polymer (Figure 2, curve a) showed the highest current response for copper(II) reduction near 0 V, confirming efficient electron transfer for this process in a noncomplexing medium. However, at more negative potentials (below -0.4 V), the current related to the direct reduction of hydrogen peroxide was minimal, indicating limited electrocatalytic performance of copper ions in the absence of the polyelectrolyte in agreement with CV data. In the case of the pAAmAA copolymer (Figure 2, curve b), a distinct and well-defined signal corresponding to the reduction of Cu^{2+} ions was observed around 0 V. At the same time, the current related to the reduction rate of hydrogen peroxide at more negative potentials (below -0.4 V) was also noticeably enhanced compared to the KNO_3 solution. In contrast, voltammetry in the PAA-based supporting electrolyte (Figure 2, curve c) resulted in a copper(II) reduction peak of similar intensity to that of the pAAmAA-based supporting electrolyte, but the current associated with direct hydrogen peroxide reduction was significantly lower. This confirms that although PAA facilitates $\text{Cu}(\text{II})$ reduction, it is less effective in the electrocatalysis of direct hydrogen peroxide reduction, making it the least favorable among the tested polyelectrolytes in such regard.

Although pAAmAA showed slight improvements in the SWV mode, it did not significantly enhance the detection limit (data not shown) compared to previous studies with PAA [20]. Consequently, an attempt to optimize further detection performances of the system, the effect of pAAmAA concentration was studied in detail. Figure 3 presents the CV curves with pAAmAA concentrations ranging from 0.5% to 5%. The voltammogram with 0.5% pAAmAA (Figure 3, curve a) exhibits the broadest and most pronounced signals corresponding to the electrode processes of copper ions at potential close to 0 V. Additionally, the current recorded at negative potentials (approximately -0.4 V and beyond) remained relatively high, with only the 1% copolymer solution (Figure 3, curve b) showing a greater response in this region. At higher pAAmAA concentrations, particularly 3% (Figure 3, curve e) and 5% (Figure 3, curve f), the reduction peak of Cu^{2+} becomes less distinct, and the overall current at negative potentials decreases. This effect may be attributed to the increased viscosity of the supporting electrolyte,

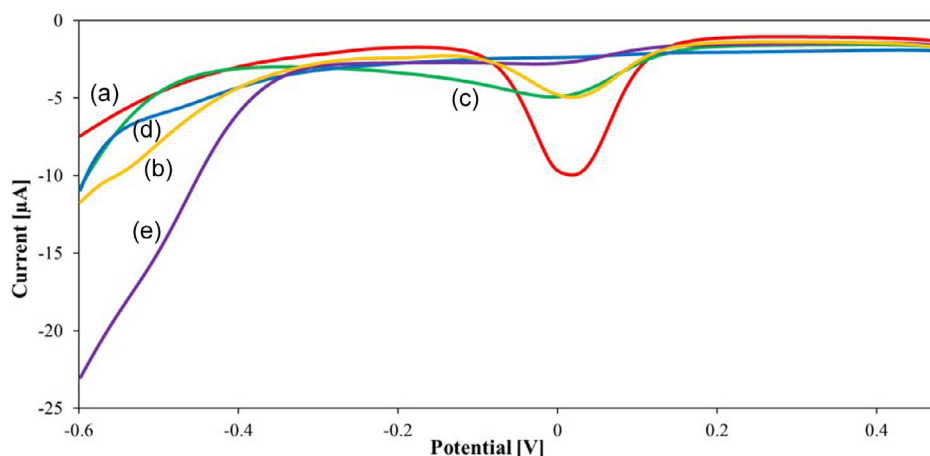


FIGURE 2 | Square wave voltammograms recorded at a GCE in selected supporting electrolytes: (a) 0.1 mol L^{-1} KNO_3 , (b) 1% (w/w) pAAmAA, (c) PAA, (d) pAMPS, and (e) neutralized pAMPS (pH 7). All solutions were prepared in 0.1 mol L^{-1} KNO_3 with 1 mM hydrogen peroxide and 2×10^{-4} mol L^{-1} copper ions(II). SW parameters: amplitude 0.05 V, frequency 8 Hz, step potential -0.005 V.

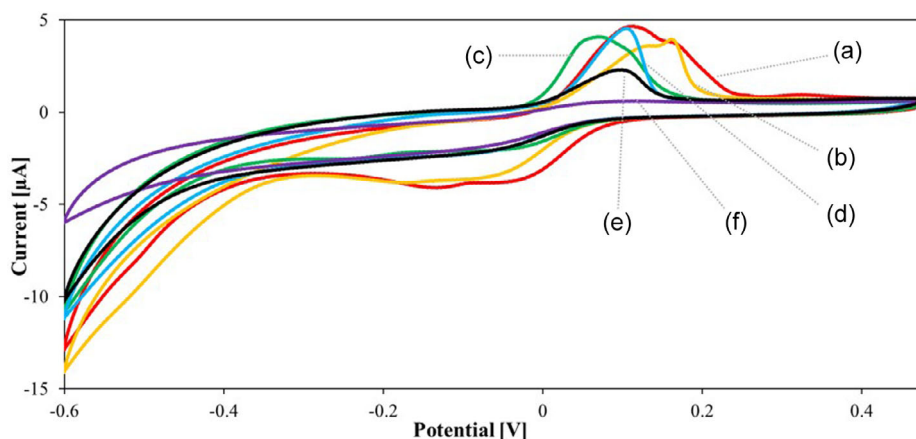


FIGURE 3 | Typical cyclic voltammograms recorded at a GCE at a scan rate of 50 mV s^{-1} for 1 mM hydrogen peroxide in the presence of $2 \times 10^{-4} \text{ mol L}^{-1}$ copper(II) ions, using a pAAmAA copolymer-based supporting electrolyte at varying mass concentrations: (a) 0.5, (b) 1, (c) 1.5, (d) 2, (e) 3, and (f) 5%, all dissolved in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$.

which could limit diffusion efficiency, leading to a reduction of the intensity of the voltammetric signals. This interpretation is supported by chronoamperometric measurements, which led to diffusion coefficient calculations using the Cottrell equation, performed for pAAmAA at concentrations between 0.5% and 5%, where the calculated diffusion coefficients progressively decreased with increasing copolymer concentration (Table S1). In contrast, intermediate concentrations of 1.5% and 2% (curves c and d, respectively) produce moderate current intensities, considering both electrode processes at about 0 and -0.4 V .

Among all tested concentrations, 1% pAAmAA (Figure 3, curve b) proved to be the most effective for direct hydrogen peroxide reduction. While it generated a slightly lower electrochemical response for copper(II) reduction, it exhibited the highest cathodic current among all studied pAAmAA concentrations, particularly at potentials more negative than -0.4 V , corresponding to the direct hydrogen peroxide reduction. This indicates that the 1% pAAmAA solution provides an optimal environment for hydrogen peroxide detection.

Having determined the optimal concentration of the pAAmAA copolymer as a supporting electrolyte for hydrogen peroxide

detection, a previously established gas-phase detection procedure [20] was applied. Gaseous hydrogen peroxide was generated by evaporation of an aqueous solution of known concentration (1×10^{-5} – $1 \times 10^{-4} \text{ mol L}^{-1}$), inserted in a sealed glass chamber, and left at room temperature for 3 h to ensure equilibration between the liquid and gas phases. Following this period, an SPE modified with the optimized pAAmAA solution as a supporting electrolyte, containing Cu^{2+} ions was introduced into the chamber via a cap, and the entrance was immediately sealed. The measurement initialization time, allowing the analyte to partition into the supporting electrolyte, was extended to 4 min compared to the previously established 3-min interval [20]. This modification accounts for the differing physicochemical properties of polymers and their ability to absorb analyte molecules from a gas phase.

Figure 4 presents SW voltammograms recorded for gaseous hydrogen peroxide within its gas-concentration range of 3.7×10^{-12} – $3.7 \times 10^{-11} \text{ mol L}^{-1}$, as calculated by means of Henry's law [31, 32]. As the hydrogen peroxide concentration increased, a corresponding rise in current intensity was observed at negative potentials, manifested as an increase in the overall

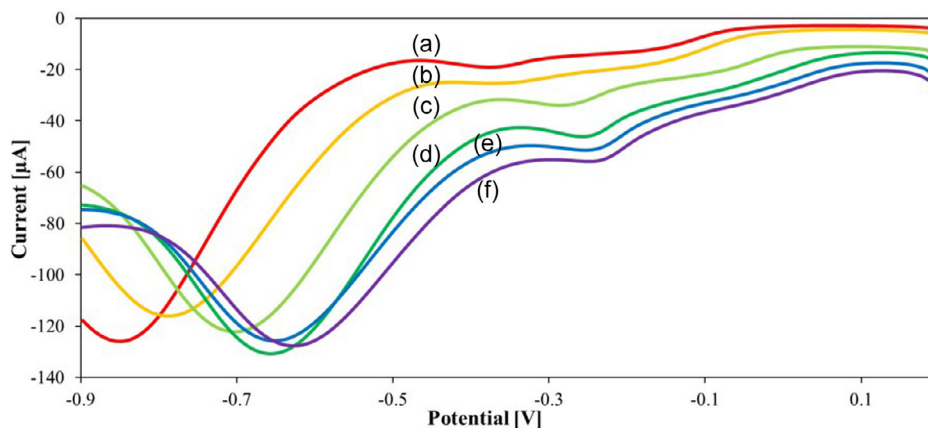


FIGURE 4 | SWV recorded at a bare carbon screen-printed electrode for selected hydrogen peroxide concentrations in the gas phase with supporting electrolyte containing 1% pAAmAA solution in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ with $2 \times 10^{-4} \text{ mol L}^{-1}$ copper(II) ions. Curves: (a) blank, (b) 3.7×10^{-12} , (c) 1.11×10^{-11} , (d) 1.85×10^{-11} , (e) 2.59×10^{-11} , (f) $3.7 \times 10^{-11} \text{ mol L}^{-1}$. SW parameters: frequency 8 Hz, SW amplitude 0.2 V, step potential -0.005 V .

background current. Compared to experiments involving direct addition of hydrogen peroxide to the supporting electrolyte, the current–concentration relationship obtained in the gas-phase setup showed a nonlinear trend. This behavior is partly influenced by the relatively large square-wave amplitude of 200 mV applied during the measurements, which affects the voltammogram shape by shifting the reductive current tail toward less negative potentials as the hydrogen peroxide concentration increases. To further validate this effect, additional SWV measurements were performed using lower amplitudes (20–200 mV), confirming a systematic enhancement of the reduction signal along with a progressive shift in peak position as the amplitude increased (Figure S4). These results demonstrate that the nonlinear response originates from amplitude-dependent kinetic and waveform effects rather than from limitations of the sensing configuration. Despite this behavior, pAAmAA demonstrates promising properties for gas-phase hydrogen peroxide detection, particularly in terms of sensitivity. Further optimization is obviously required to enhance reproducibility and fully explore the analytical potential of this copolymer.

3.2 | pAMPS

According to the literature, pAMPS in its native acidic form (pH 1.5) demonstrates strong complexing properties, rapidly binding Cu^{2+} ions and substantially reducing their catalytic activity [33, 34]. Thus, in accord with the literature data, pAMPS strongly diminishes the copper signal near 0 V (Figure 1, curve d). In addition, the lack of freely available catalyst led to a diminished direct reduction of hydrogen peroxide, manifested in a relatively low current response at negative potentials (e.g., more negative than -0.4 V). Neutralizing the functional groups of pAMPS with NaOH improved the availability of Cu^{2+} in solution, significantly enhancing direct hydrogen peroxide reduction at potentials more negative than -0.4 V (Figure 1, curve e). This effect is manifested as a marked increase in the current at negative potentials, even surpassing the enhancement observed with PAA, which highlights the superior catalytic efficiency of neutralized pAMPS. Additionally, a shift of the hydrogen peroxide reduction potential toward less negative values was observed,

supporting the electrocatalytic features of the neutralized pAMPS solution.

Analogously, the next step involved verifying the results using SWV to gain further insights into the electrochemical behavior (Figure 2). The complexation of copper(II) ions by native pAMPS was confirmed again by the relatively diminished signal around 0 V, corresponding to the electrode reactions of copper (Figure 2, curve d). However, the presence of pAMPS also led to an increased current at more negative potentials, associated with the direct reduction of hydrogen peroxide. Interestingly, the reduction signal of Cu^{2+} near 0 V in neutralized pAMPS (Figure 2, curve e) showed only a slight increase compared to its acidic form, yet a significant enhancement of the cathodic tail was observed.

To directly assess how native pAMPS affects the electrochemical availability of Cu^{2+} , square-wave voltammetric titration experiments were performed in a $\text{KNO}_3/\text{Cu}^{2+}$ electrolyte, while gradually increasing the concentration of pAMPS (Figure S5). In the blank solution, a well-defined Cu^{2+} reduction peak was observed around 0 V. Upon addition of pAMPS, the peak current decreased systematically with polymer concentration, and the peak potential exhibited a slight shift toward more negative values. At concentrations close to 1% pAMPS, the conditions used in the sensing experiments, the Cu^{2+} reduction signal was almost completely suppressed, confirming a substantial decrease in electrochemically accessible Cu^{2+} ions due to complexation.

The calibration curve for hydrogen peroxide detection in the aqueous phase was constructed using a native 1% pAMPS solution. Despite challenges related to the complexation of copper(II) ions, the detection limit was successfully lowered to the micromolar range (data not shown). However, poor repeatability due to copper ion complexation hindered the statistical reliability of gas-phase detection.

For these reasons, optimization of the pAMPS solution was carried out by adjusting the pH value to uncover a more favorable environment for gas-phase detection. The effect of pH on the polymer's performance was systematically investigated over a range from 2 to 9.8 using the SWV technique. The reduction signal of copper(II) ions reached its maximum at pH 4.4, as illustrated in Figure 5. Below and above these pH values, the signal

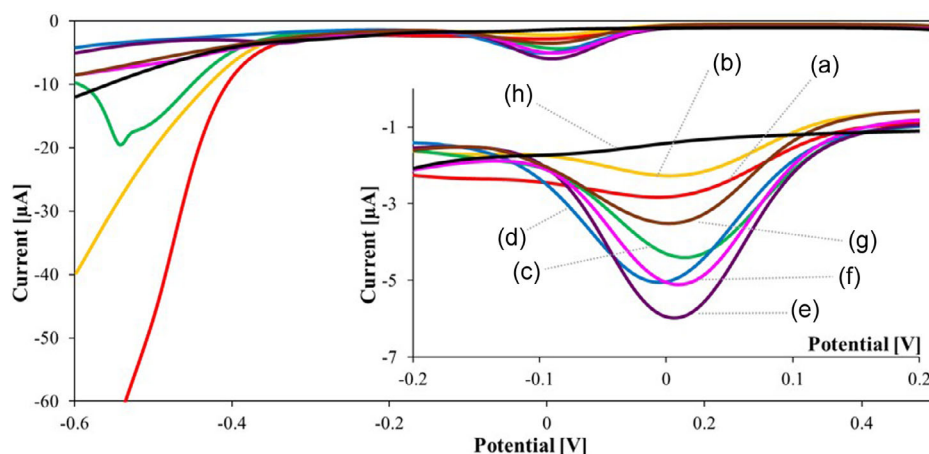


FIGURE 5 | SW voltammograms recorded at a GCE in 1% pAMPS at different pH values: (a) 2, (b) 2.5, (c) 3.5, (d) 4, (e) 4.44, (f) 6, (g) 7, and (h) 9.8. All solutions contained 1 mM hydrogen peroxide and 2×10^{-4} mol L^{-1} copper(II) ions. Inset: enlarged section showcasing redox reactions of copper(II) ions. SW parameters as in Figure 2.

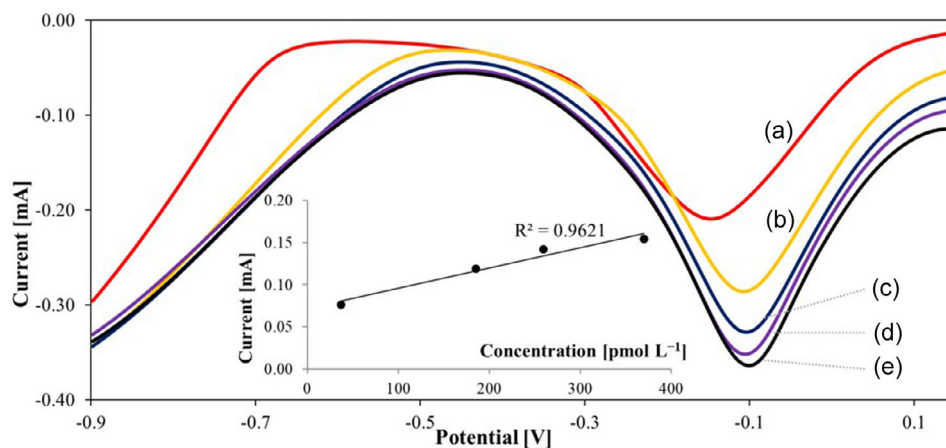


FIGURE 6 | Effect of gaseous hydrogen peroxide presence recorded with SW voltammetry at a Prussian blue-modified SPE: (a) blank, (b) 3.7×10^{-11} , (c) 1.85×10^{-10} , (d) 2.59×10^{-10} , (e) 3.7×10^{-10} mol L⁻¹. The supporting electrolyte consisted of 1% pAMPS (pH) 2 with 2×10^{-4} mol L⁻¹ copper(II) ions. Inset: calibration curve of the relative current gain at the Prussian blue reduction potential upon hydrogen peroxide concentration increment. SW parameters as in Figure 4.

diminished, reaching a minimum in alkaline solutions. At strongly negative potentials, where the direct hydrogen peroxide takes place, the electrolyte at pH 2 (curve a) exhibited the highest current compared to other pH values. The significant increase of the current at low pH can likely be attributed to enhanced hydrogen evolution, though this effect was not observed in the native pAMPS solution at pH 1.5. Solutions at other pH levels exhibited considerably lower current values at strongly negative potentials, leading to the selection of pAMPS at pH 2 for further investigation.

To boost further the electrocatalytic effect and the overall analytical performances, the optimized pAMPS supporting electrolyte at pH 2 was applied in combination with PB-modified SPEs. PB is widely recognized as an efficient electrocatalyst for the reduction of hydrogen peroxide, owing to its excellent redox properties, chemical stability, and compatibility with SPEs. This well-established catalytic activity has led to its frequent use in electrochemical sensors for H₂O₂. In our previous study [18], PB-modified SPEs demonstrated superior performance for hydrogen peroxide detection, particularly based on the electrode reaction for the direct reduction of hydrogen peroxide, due to synergistic interactions with copper(II) ions and PB. Exemplary relative standard deviation (RSD) from analysis of hydrogen peroxide in liquid phase is given in Table S2. These results strongly supported the application of PB-modified electrodes in the current gaseous system.

In the present work, the PB-modified SPE demonstrated the best performance, showing significant improvements in sensitivity and reproducibility. A repeatable linear relationship was observed between the recorded current and hydrogen peroxide concentration in the gas phase within the range of 3.7×10^{-11} – 3.7×10^{-10} mol L⁻¹ (Figure 6, inset). The limit of quantification (LOQ, 2.92×10^{-11} mol L⁻¹) was calculated from the calibration curve using the formula kSD/b , where $k = 10$, SD represents the standard deviation of the intercept, and b is the slope of the calibration curve. A comparison of the obtained detection and quantification limits with representative literature reports is summarized in Table 1. To assess the reproducibility of

the method, repeated measurements were performed for a gas-phase concentration range as given for the linear range. The RSD for six consecutive detections was determined to be 4.7%, with an average value for any concentration studied not exceeding 5%. Recovery studies for hydrogen peroxide detection yielded results ranging from 88.4% to 112.4% across the linear calibration range. The stability of the signal studied within a 3-month period with the use of a new sensor each time was assessed with RSD ranging between 0.98% and 2.06% for any studied concentration within the linear range. These enhancements align with previous findings [45] and literature reports on the electrocatalytic properties of PB toward hydrogen peroxide reduction. Additionally, the synergistic interaction between PB and copper(II) ions facilitates indirect hydrogen peroxide detection, further improving the system's analytical performance [47].

3.3 | pAAmAA: pAMPS Mix

Taking into account the two previously described polyelectrolytes as potential supporting electrolytes for gaseous hydrogen peroxide sensing, we also evaluated their combined use. A supporting electrolyte containing equal mass percent of both polymers (1%) dissolved in 0.1 mol L⁻¹ KNO₃, along with 2×10^{-4} copper(II) ions as an electrocatalyst, was prepared. The pAMPS–pAAmAA mixture demonstrated promising performance for direct hydrogen peroxide detection in an aqueous environment using GCE. SWV measurements revealed a linear increase in current with hydrogen peroxide concentrations ranging from 1×10^{-4} to 5×10^{-3} mol L⁻¹ (data not shown). Gas-phase studies were conducted using both bare and PB-modified SPEs. The results suggest that the combination of PB-SPE with pAMPS–pAAmAA provides an optimized system for gaseous hydrogen peroxide detection. This approach enables sensitivity down to 1.8×10^{-10} mol L⁻¹, highlighting its potential for highly sensitive electrochemical sensing applications. The repeatability was at an acceptable level (8.4% at 3.7×10^{-10} mol L⁻¹), but sensitivity in comparison to pAMPS pH 2 was lower.

TABLE 1 | Overview of electrochemical detection and quantification limits in relation to values reported in the literature.

Electrode sensor	Method	LOD, mol L ⁻¹	Linear range, mol L ⁻¹	Phase	References
GCE	SWV	1.2×10^{-4}	1×10^{-4} – 1×10^{-3} 1×10^{-3} – 7×10^{-3}	Gas	[20]
SPE	Amperometry	1.6×10^{-8}	2.94×10^{-7} – 2.94×10^{-6}	Gas	[35]
PB-GCE	Amperometry	3.0×10^{-7}	5×10^{-7} – 1×10^{-3}	Liquid	[36]
PBNCs/rGO-GCE	Amperometry	4.5×10^{-8}	5×10^{-8} – 1.2×10^{-4}	Liquid	[37]
PB-SPE	Amperometry	4.0×10^{-7}	4×10^{-7} – 1×10^{-4}	Liquid	[38]
PEI/Rh-NP-SPE	Amperometry	2.0×10^{-6}	5×10^{-6} – 6×10^{-4}	Liquid	[39]
Hb-Au-SPE	Amperometry	5.5×10^{-6}	—	Liquid	[40]
AgNP@GNR/SPE	Amperometry	2.0×10^{-5}	5×10^{-5} – 1.8×10^{-3} 1.8×10^{-3} – 5×10^{-3}	Liquid	[41]
PBNPs-SPE	Amperometry	2.0×10^{-5}	2×10^{-5} – 7×10^{-4}	Liquid	[42]
Ti ₃ C ₂ T _x MXene/FCN-SPCE	CV	1.2×10^{-10}	1.5×10^{-8} – 8.8×10^{-7}	Gas	[43]
PAA-SPE	CV	5.9×10^{-8}	4.4×10^{-7} – 3.6×10^{-6}	Gas	[44]
PB-SPE	SWV	2.3×10^{-6}	1×10^{-5} – 1×10^{-3}	Liquid	[45]
NiCo ₂ Se ₄ /GC	SWV	—	1.22×10^{-11} – 6.1×10^{-11}	Gas	[46]
pAMPS-PB-SPE	SWV	8.7×10^{-12}	3.7×10^{-11} – 3.7×10^{-10}	Gas	This work

Abbreviations: AgNP, silver nanoparticles; GNR, graphene nanoribbons; Hb, hemoglobin; PBNPs, Prussian blue nanocubes; PEI, polyethyleneimine; rGO, reduced graphene oxide; Rh-NP, rhodium nanoparticles.

4 | Conclusions

This study systematically evaluated the role of polyelectrolytes as supporting electrolytes in the electrochemical detection of hydrogen peroxide using copper(II)-mediated catalysis. Through comparative analysis, pAMPS and pAAMAA were identified as promising alternatives to PAA. The strong complexation of Cu²⁺ by native pAMPS initially limited its catalytic efficiency; however, adjusting the pH to 2 restored its effectiveness by minimizing metal chelation. The 1% pAAMAA solution was considered optimal for direct H₂O₂ reduction, and the pAMPS–pAAMAA mixture also demonstrated satisfactory performance in combination with PB-modified electrodes. Nonetheless, comparative evaluation favored pAMPS at pH 2 as the final choice.

Gas-phase studies confirmed that the optimized polyelectrolyte-based electrolytes facilitated highly sensitive detection of hydrogen peroxide, achieving a detection limit of 8.77×10^{-12} mol L⁻¹. The improved performance was attributed to enhanced analyte repartitioning and electrocatalytic interactions with Cu²⁺ and PB. Despite these advancements, variability in signal response and background current fluctuations remain challenges that require further optimization.

Future research will focus on refining the electrolyte composition to enhance stability, reproducibility, and overall analytical performance. Additionally, exploring the integration of polyelectrolytes with emerging voltammetric techniques like square-wave amperometry [48–52] and differential square-wave voltammetry [53–55] may further improve sensitivity and expand applications in environmental monitoring and biomedical diagnostics. These findings demonstrate the potential of polyelectrolyte-enhanced electrochemical sensors as a viable alternative for real-time hydrogen peroxide detection, particularly in challenging gas-phase environments.

Author Contributions

Conceptualization D.G., V.M.; Data curation B.B.; Formal analysis B.B.; Funding acquisition V.M.; Investigation B.B., N.U., D.G.; Methodology D.G., V.M.; Project administration D.G.; Supervision D.G., V.M.; Validation D.G.; Visualization B.B., N.U.; Writing – original draft B.B., D.G., V.M.; Writing – review & editing B.B., D.G., V.J., K.K., S.S., V.M.

Acknowledgments

This research was funded in whole or in part by National Science Center, Poland 2020/39/I/ST4/01854. V.J. would like to acknowledge funding from the Slovenian Research And Innovation Agency, programs P2-0421 and P2-0393, and projects N1-0224 and J2-50076. For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

Funding

This work was supported by Narodowe Centrum Nauki (2020/39/I/ST4/01854), and Slovenian Research And Innovation Agency (P2-0421, P2-0393, N1-0224 and J2-50076).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Supporting Fig. S1:** Calculated Tafel slopes derived from linear sweep voltammetry (LSV) measurements (scan rate: 5 mV s^{-1}) recorded at bare screen-printed electrode for (a) 1% PAA with H_2O_2 (1 mM) and (b) 1% PAA with Cu^{2+} ($2 \times 10^{-4} \text{ mol L}^{-1}$) and H_2O_2 (1 mM). Each solution contained 0.1 M KNO_3 . **Supporting Fig. S2:** EIS of Prussian blue screen-printed electrode recorded in 0.1 M KNO_3 (green, full circles) and the presence $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ (blue, empty circles). **Supporting Fig. S3:** SW voltammograms recorded at a Prussian blue screen printed electrode in 0.1 M KNO_3 and 1% PAA as supporting electrolyte (a, d), in the presence of $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ (b, c, e, f) and increasing concentration of H_2O_2 : (c) 0.5, (d, e) 1, and (f) 8 mM. SW parameters: frequency 8 Hz, SW amplitude 0.2 V, step potential -0.005 V . **Supporting Fig. S4:** SW voltammograms recorded in the gas-phase using bare screen-printed electrode for 1% pAaMAA in the presence of Cu^{2+} ions ($2 \times 10^{-4} \text{ mol L}^{-1}$) and hydrogen peroxide (10 mM) at different amplitudes: 20 mV (a), 50 mV (b), 75 mV (c), 100 mV (d), 150 mV (e), and 200 mV (f). Frequency 8 Hz. **Supporting Fig. S5:** SW voltammograms recorded at a GCE in $\text{KNO}_3/\text{Cu}^{2+}$ supporting electrolyte with increasing concentrations of native pAMPS: (a) blank, (b) 0.002%, (c) 0.004%, (d) 0.01%, (e) 0.03%, (f) 0.4%, (g) 0.7%, and (h) 1%. All solutions contained $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$. SW parameters: amplitude 50 mV, frequency 8 Hz. **Supporting Table S1:** Diffusion coefficients calculated using the Cottrell equation via chronoamperometric measurements in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system at different pAaMAA concentrations. **Supporting Table S2:** Calculated RSD for the results of SWV measurements recorded for hydrogen peroxide in the concentration range of 0.001 - 0.1 mM in pAMPS at pH 2 with the addition of copper (II) ions ($2 \times 10^{-4} \text{ mol L}^{-1}$). Measurements were performed in the liquid phase.

Supplementary material

Polyelectrolyte-Enhanced Electrochemical Sensing of Gaseous Hydrogen Peroxide with Copper(II)– Mediating Systems

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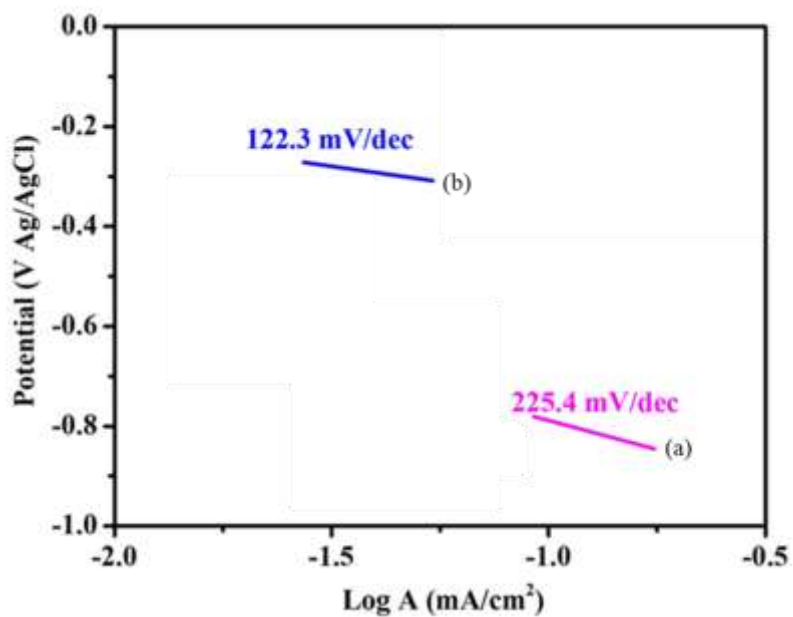


Fig. S1 Calculated Tafel slopes derived from linear sweep voltammetry (LSV) measurements (scan rate: 5 mV s⁻¹) recorded at bare screen-printed electrode for (a) 1% PAA with H₂O₂ (1 mM) and (b) 1% PAA with Cu²⁺ (2×10^{-4} mol L⁻¹) and H₂O₂ (1 mM). Each solution contained 0.1 M KNO₃.

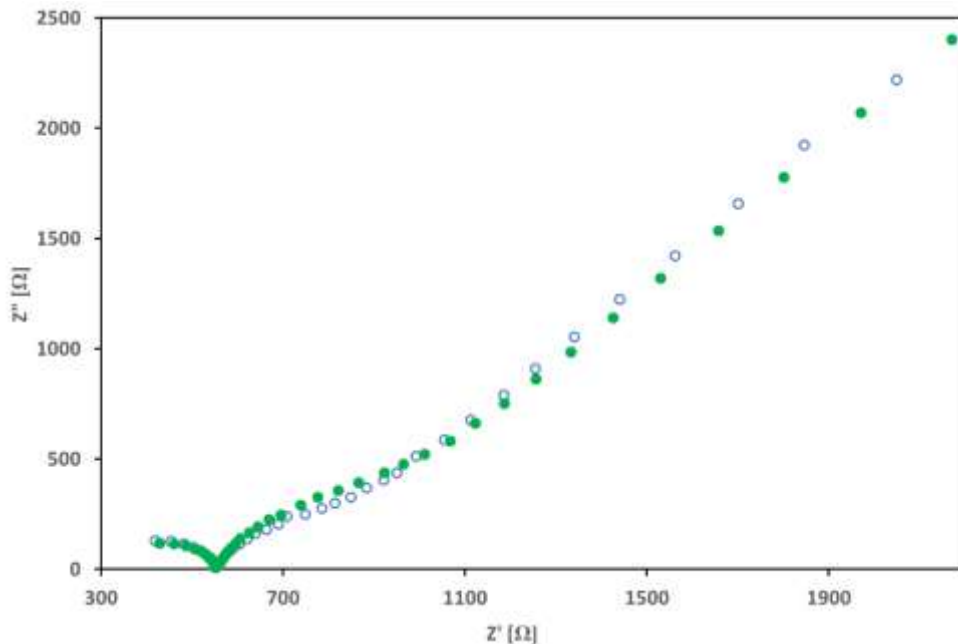


Fig. S2 EIS of Prussian blue screen-printed electrode recorded in 0.1 M KNO₃ (green, full circles) and the presence 2×10^{-4} mol L⁻¹ Cu²⁺ (blue, empty circles).

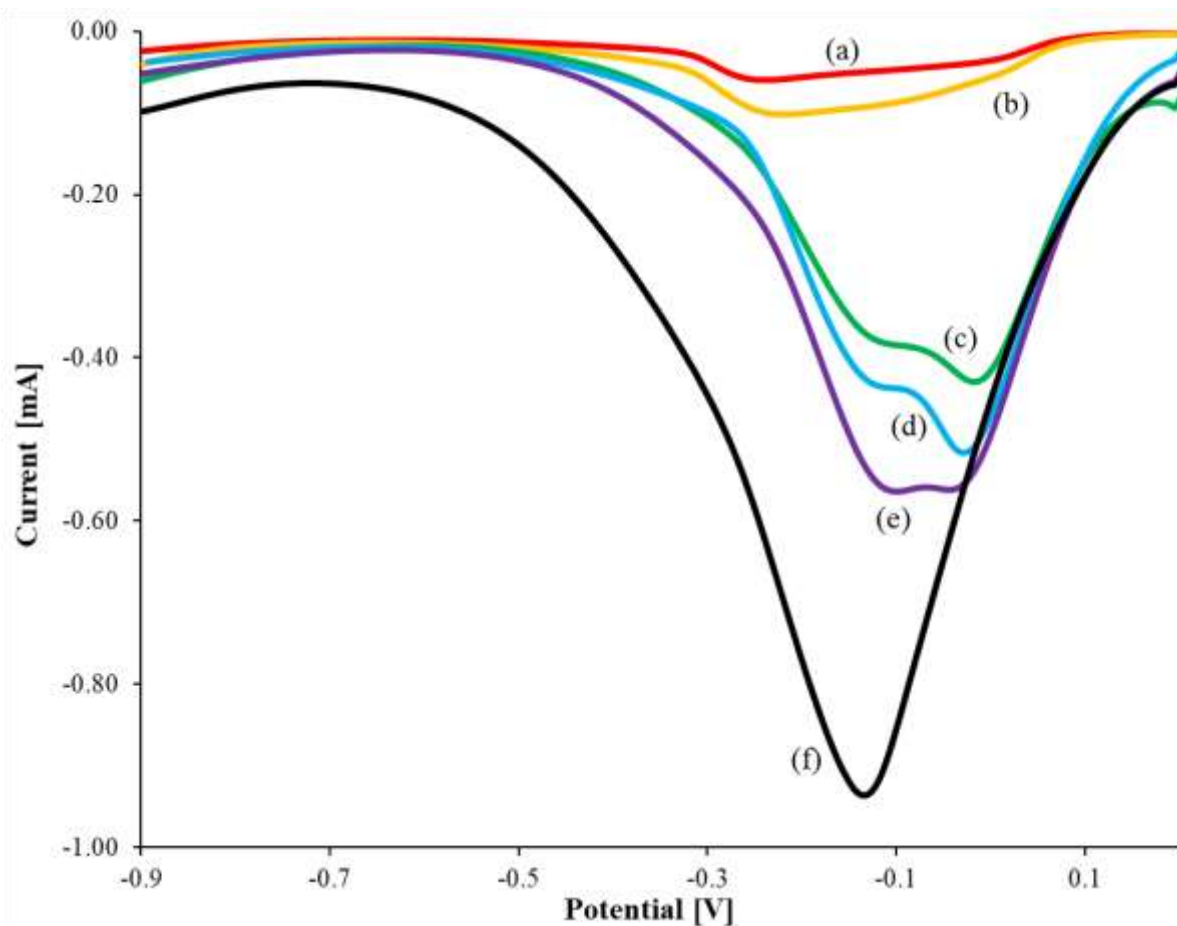


Fig. S3 SW voltammograms recorded at a Prussian blue screen printed electrode in 0.1 M KNO_3 and 1% PAA as the supporting electrolyte (a, d), in the presence of $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ (b, c, e, f) and increasing concentration of H_2O_2 : (c) 0.5, (d, e) 1, and (f) 8 mM. SW parameters: frequency 8 Hz, SW amplitude 0.2 V, step potential -0.005 V .

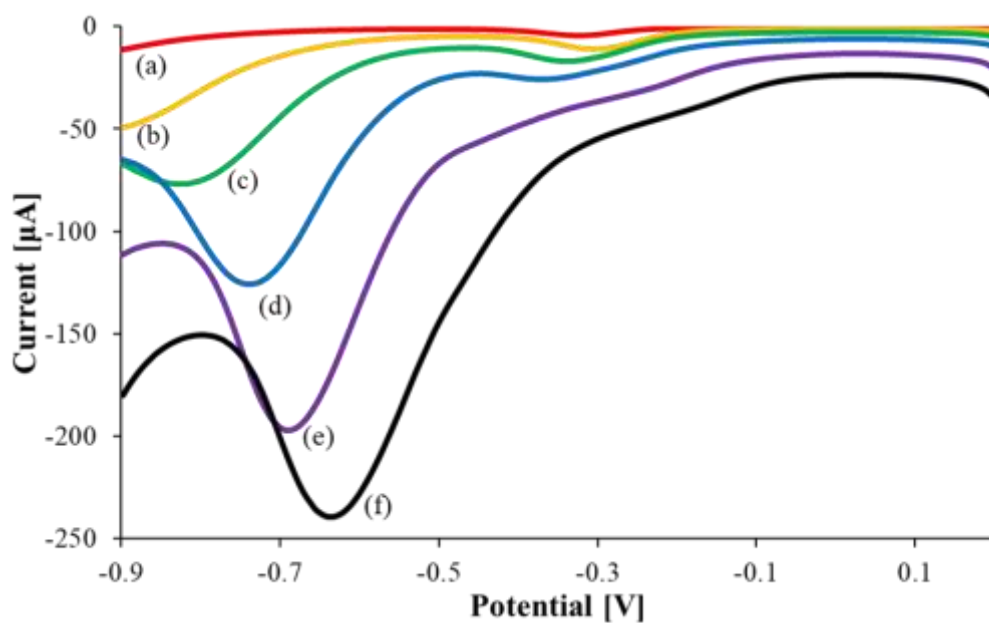


Fig. S4 SW voltammograms recorded in the gas-phase using bare screen-printed electrode for 1% pAAmAA in the presence of Cu^{2+} ions ($2 \times 10^{-4} \text{ mol L}^{-1}$) and hydrogen peroxide (10 mM) at different amplitudes: 20 mV (a), 50 mV (b), 75 mV (c), 100 mV (d), 150 mV (e), and 200 mV (f). Frequency 8 Hz.

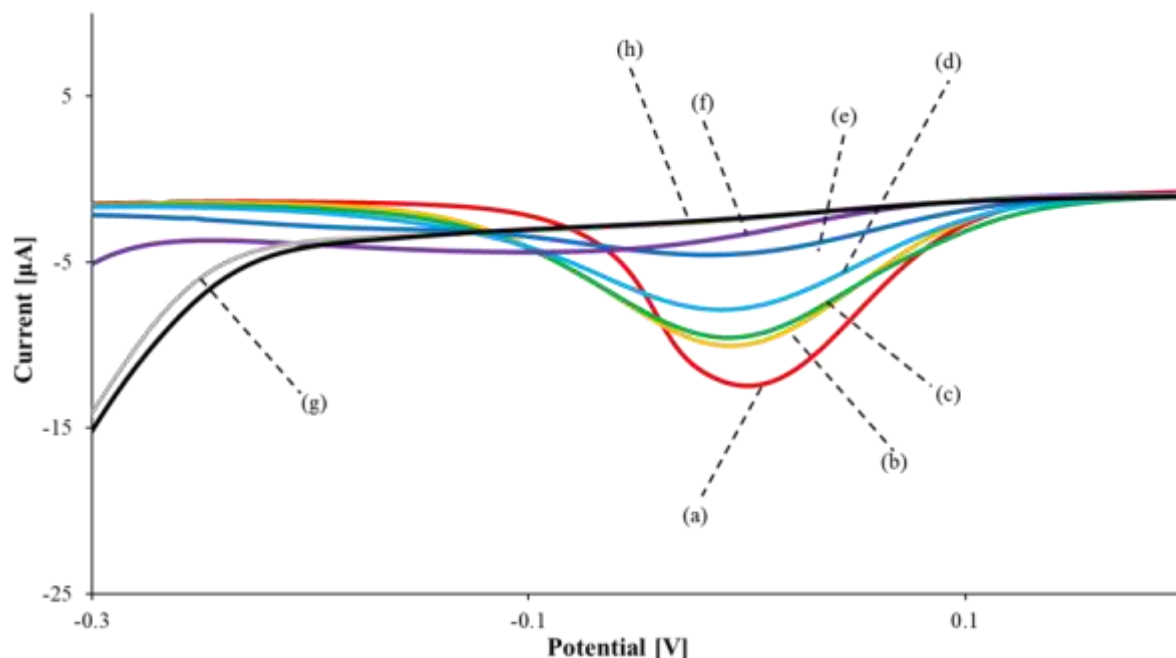


Fig. S5 SW voltammograms recorded at a GCE in $\text{KNO}_3/\text{Cu}^{2+}$ supporting electrolyte with increasing concentrations of native pAMPS: (a) blank, (b) 0.002%, (c) 0.004%, (d) 0.01%, (e) 0.03%, (f) 0.4%, (g) 0.7%, and (h) 1%. All solutions contained $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$. SW parameters: amplitude 50 mV, frequency 8 Hz.

Table S1 Diffusion coefficients calculated using the Cottrell equation via chronoamperometric measurements in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system at different pAAmAA concentrations

Polymer concentration	$D_{\text{ox}} [\text{cm}^2 \text{ s}^{-1}]$
0.50%	6.45×10^{-6}
1%	5.99×10^{-6}
2%	4.91×10^{-6}
3%	4.78×10^{-6}
5%	1.56×10^{-6}

Table S2. Calculated RSD for the results of SWV measurements recorded for hydrogen peroxide in the concentration range of 0.001 - 0.1 mM in pAMPS at pH 2 with the addition of copper (II) ions (2×10^{-4} mol L⁻¹). Measurements were performed in the liquid phase.

Concentration [mM]	RSD
0.001	4.44
0.005	8.02
0.007	6.03
0.030	5.10
0.050	5.32
0.100	5.41

Microchemical Journal

Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface

--Manuscript Draft--

Manuscript Number:	MICROC-D-26-05708R1
Article Type:	Research Paper
Section/Category:	Electrochemical methods and electrochemical-based sensors
Keywords:	voltammetry; three-phase junction; hydrogen peroxide; gas detection
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Abstract:	Hydrogen peroxide present in the gas phase is an important target analyte in environmental monitoring, industrial process control, and non-invasive diagnostics. In this study, a simple and sensitive electrochemical platform for the direct detection of gaseous H₂O₂ at a three-phase interface is presented. The proposed system is based on direct contact between gaseous hydrogen peroxide, an aqueous electrolyte phase, and the electrode surface, enabling efficient electrochemical transduction without the need for complex sample preparation or advanced membrane architectures. The aqueous phase consisted solely of KNO₃ supporting electrolyte and Cu(II) ions, providing a remarkably simple experimental configuration. The influence of electrode material, electrolyte composition, and voltammetric methodology on the analytical response was systematically investigated. By combining an optimized three-phase interface with advanced voltammetric techniques, enhanced sensitivity, favorable signal stability, and reliable trace-level quantification of gaseous H₂O₂ were achieved. The developed approach demonstrates improved analytical performance compared with previously reported configurations and highlights the practical applicability of three-phase electrochemical systems for direct gas-phase sensing.

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface

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Abstract

Hydrogen peroxide present in the gas phase is an important target analyte in environmental monitoring, industrial process control, and non-invasive diagnostics. In this study, a simple and sensitive electrochemical platform for the direct detection of gaseous H_2O_2 at a three-phase interface is presented. The proposed system is based on direct contact between gaseous hydrogen peroxide, an aqueous electrolyte phase, and the electrode surface, enabling efficient electrochemical transduction without the need for complex sample preparation or advanced membrane architectures. The aqueous phase consisted solely of KNO_3 supporting electrolyte and Cu(II) ions, providing a remarkably simple experimental configuration. The influence of electrode material, electrolyte composition, and voltammetric methodology on the analytical response was systematically investigated. By combining an optimized three-phase interface with advanced voltammetric techniques, enhanced sensitivity, favorable signal stability, and reliable trace-level quantification of gaseous H_2O_2 were achieved. The developed approach demonstrates improved analytical performance compared with previously reported configurations and highlights the practical applicability of three-phase electrochemical systems for direct gas-phase sensing.

Keywords: voltammetry; three-phase junction; hydrogen peroxide; gas detection

1. Introduction

The concept of the three-phase boundary (TPB) is fundamental in electrochemistry, encompassing a wide range of systems in which a solid electrode is in contact with multiple phases, such as immiscible liquids, different solid phases, or gas–liquid interfaces [1, 2]. In such systems, electrochemical reactions are mainly confined to regions, where all three phases are in direct contact, making the TPB the true locus of charge transfer. This is exemplified by classical systems such as the standard hydrogen electrode, as well as by modern energy technologies, including fuel cells and gas diffusion electrodes, where the availability and structure of TPB regions critically determine overall performance [3-5].

The importance of TPB extends to heterogeneous electrocatalysis involving solid catalysts, particularly when these are present as micro- or nanoparticles immobilized on electrode surfaces [6-8]. In such cases, efficient electrocatalytic turnover requires the simultaneous availability of electronic conduction through the solid phase, ionic transport through the electrolyte, and access of reactants at the three-phase boundary.

A particularly illustrative and well-defined model system is provided by the voltammetry of solid particles, developed by Fritz Scholz [9]. In this approach, insoluble electroactive solid particles immobilized on an electrode surface establish a distinct three-phase boundary with the electrode and the supporting electrolyte. These systems offer a controlled framework for probing the mechanistic aspects of electrochemical reactions at TPB sites and serve as compelling model examples that highlight the fundamental importance of three-phase interfaces in electrochemistry.

In the same context, three-phase droplet electrodes are of particular relevance [10, 11]. These systems consist of a solid electrode in contact with two immiscible liquid phases and enable the investigation of electrode reactions coupled with simultaneous ion transfer across liquid–liquid interfaces. Such sophisticated configurations have enabled significant advances in understanding both the thermodynamics and kinetics of ion transfer processes [12-16].

Despite these advances, the utilization of three-phase electrode configurations for analytical applications involving gaseous analytes remains largely unexplored [5, 17] compared to conventional two-phase (solid–liquid or solid–gas) sensors. In the present communication, we demonstrate that a simple three-phase electrochemical setup, comprising a conventional solid graphite electrode, an aqueous electrolyte, and an air phase, can be effectively employed for the ultra-trace determination of hydrogen peroxide in the gas (air) phase (Scheme 1). This

system introduces a conceptually new approach for the design of electrochemical gas sensors for H₂O₂ detection and quantification.

Hydrogen peroxide is routinely employed as an oxidizing agent in chemical, pharmaceutical, and food-related processes [18-25], while in biological systems it acts as both a product of oxidase-driven reactions and a signalling mediator involved in redox regulation [26-29]. Its concentration is therefore frequently used as an indirect marker of enzymatic activity and metabolic state [26, 30, 31]. In the respiratory tract, elevated levels of H₂O₂ in exhaled breath have been correlated with pathological conditions, including asthma and lung cancer [32-35], which motivates the development of reliable methods for its detection in the gas phase. For gaseous H₂O₂ analysis, spectroscopy and colorimetry remain the most established approaches [36-39], although their practical implementation is often limited by instrumental complexity and insufficient suitability for real-time measurements. In this context, electrochemical techniques, particularly amperometry [40] and voltammetry [41], offer a viable alternative due to their sensitivity, operational simplicity, and compatibility with miniaturized systems [42], making them attractive for direct and on-site detection.

Electrochemical techniques, despite their many advantages, are not free from certain limitations, particularly when it comes to reaching the lowest detectable concentrations of an analyte. Such constraints often arise from the applied measurement technique, the nature of supporting reagents, or the intrinsic current response of the system. For this reason, there is a continuous effort to develop new electroanalytical methodology that enable reliable detection at ever-decreasing levels. One promising solution is the implementation of a three-phase measurement system, as described in the present communication. The triple-phase junction region depicted in Scheme 1 represents the location where gaseous analyte, ionic charge carriers, and the solid electrode surface coexist [10, 43]. As a result, electrochemical reactions of the gaseous analyte is confined to the highly localized and well-accessible three-phase junction zone, which favours efficient mass transport of the gas analyte and enhances the analytical response [44]. In this arrangement, gaseous H₂O₂ used as an analyte can directly reach the electrode surface, while ionic conduction is simultaneously maintained by the liquid electrolyte, effectively mitigating issues such as catalyst wetting, bubble accumulation, or blockage of active sites [45]. In contrast to our previously reported conventional two-phase sensing systems [46-50], in which gaseous hydrogen peroxide must first dissolve in the supporting electrolyte and subsequently diffuse toward the electrode surface before electrochemical detection can occur, the proposed three-phase configuration enables direct interaction of gaseous hydrogen peroxide with the gas-accessible electrode/electrolyte

interface, thereby eliminating the intermediate dissolution-controlled transfer step. This fundamentally changes the mode of analyte transport and access to the electrode surface, while simultaneously reducing the time required for electrochemical analysis. Consequently, the proposed methodology provides several important advantages, including a more efficient supply of gaseous reactants, improved accessibility of the active sensing region, the possibility of regulating the local interfacial environment, suppression of competing side reactions, and enhanced selectivity toward target electrochemical processes. As a result, the three-phase system bears a promise not only to improve sensitivity and accuracy, but also to provide a more realistic representation of gas-involved electrochemical processes, aligning with broader research directions observed in electrocatalysis, fuel cells, and sensing applications [51, 52].

To further enhance the sensitivity and mechanistic insight of H_2O_2 detection we have employed conventional square-wave voltammetry (SWV) [53], as well as recently developed advanced techniques, including electrochemical faradaic spectroscopy (EFS) [54] and differential square-wave voltammetry (DSWV) [55]. These methodologies provide several notable benefits over traditional approaches. They allow for enhanced separation of faradaic signals from background currents, improved sensitivity toward both rapid and kinetically sluggish electrode processes, and the simultaneous acquisition of mechanistic and kinetic information within a single experiment [54-56]. Together, the combination of a deliberately engineered three-phase interface and advanced pulse-based electrochemical techniques provides a new platform for highly sensitive and mechanistically informative detection of gaseous H_2O_2 .

2. Experimental

All chemicals used from Sigma-Aldrich were of analytical grade and were used without further purification. Stock solutions of KNO_3 (0.1 mol L^{-1}), CuSO_4 (0.1 mol L^{-1}), and H_2O_2 at various concentrations (1×10^{-1} , 1×10^{-3} , and $5 \times 10^{-5} \text{ mol L}^{-1}$) were prepared with deionized water produced using a Polwater DL-3 purification system. To obtain 1% (mass percentage) solutions of polyacrylic acid (PAA, average molecular weight approximately $450,000 \text{ g mol}^{-1}$) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (pAMPS, average molecular weight approximately $2,000,000 \text{ g mol}^{-1}$), 1 g of the respective polymer was dissolved in 0.1 mol L^{-1} KNO_3 solution.

Gas-liquid-solid three-phase measurements were carried out using a plastic chamber with a total volume of 150 mL, equipped with four holes in the lid. Inside the chamber, a small

electrochemical cell containing 10 mL of supporting electrolyte ($0.1 \text{ mol L}^{-1} \text{ KNO}_3$ with $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu(II)}$ ions) was placed. The reference electrode (Ag/AgCl) and the auxiliary electrode (platinum wire) were immersed in the electrolyte, whereas the working electrode was positioned to barely touch the electrolyte surface, thereby forming a three-phase contact line between the gaseous phase containing H_2O_2 , the liquid supporting electrolyte, and the solid working electrode (Scheme 1). Several types of working electrodes were initially tested, including gold and copper meshes, gold and platinum wires, paraffin-impregnated graphite rod ($\varnothing = 6 \text{ mm}$), and a glassy carbon rod ($\varnothing = 5 \text{ mm}$), in order to identify a material that ensured stable formation of the three-phase contact line together with reproducible electrochemical response. The comparison focused on signal stability, background current behaviour, susceptibility to hydrogen evolution, and overall analytical sensitivity. Based on these criteria, the glassy carbon rod was selected for the final measurements due to its superior stability, higher current response, and reliable maintenance of the three-phase interface.

In addition to the electrochemical cell, 5 mL of H_2O_2 aqueous solution was placed separately inside the chamber, outside the electrochemical vessel, to serve as an aqueous medium for vaporizing H_2O_2 . The chamber was then usually left for 30 minutes to establish equilibrium between the liquid and gas phases. Through this equilibration, the gaseous H_2O_2 concentration was calculated according to Henry's law [57, 58]. Blank measurements were carried out under identical conditions but without the addition of H_2O_2 , with the chamber maintained for the same equilibration time prior to measurement. After each experiment, the working electrode was electrochemically conditioned in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ solution using cyclic voltammetry in the potential range from 0.1 to 0.6 V using 30 consecutive cycles at a scan rate of 0.05 V s^{-1} .

Unless otherwise stated, the reported current values correspond to background-corrected signals, calculated as the net faradaic response of the sample after subtraction of the blank (hereafter referred to as relative current).

All electrochemical experiments, including cyclic, square-wave, differential square-wave voltammetry, and electrochemical faradaic spectroscopy, were performed using an Autolab PGSTAT 302N potentiostat controlled by Nova software (v. 2.1.5, Metrohm-Autolab, Netherlands). The analytical current was sampled at a fixed potential of -0.6 V versus Ag/AgCl.

SWV measurements were carried out with a frequency of 8 Hz, pulse amplitude of 0.05 V, and step potential of -5 mV . EFS measurements were carried out under square-wave chronoamperometric conditions at a mid-potential of -0.6 V , using a square-wave frequency of 50 Hz and a pulse amplitude of 0.05 V. The experiment consisted of 30 potential cycles, where

each cycle comprised two successive pulses of opposite polarity, analogous to square-wave voltammetry. Within each pulse, the current was sampled 60 times and subsequently averaged over last four consecutive points to improve the signal-to-noise ratio. For each potential cycle (defined by its serial number), forward and backward current components were determined from the respective pulses, while the net EFS signal was calculated as their difference. These components were then analyzed as a function of the serial number of the potential cycles. Although the technique is chronoamperometric in nature - thus the forward and backward currents exhibit the expected decay with time - the net current reaches a quasi-steady-state regime, analogous to microelectrode behavior, and remains significantly higher than that observed in conventional chronoamperometry [54]. For quantitative purposes, net currents obtained from the last five potential cycles were averaged and used as the analytical signal. Subtraction of the blank signal was performed throughout the experiments.

DSWV experiments were performed using a composite potential modulation scheme in which each cycle consisted of two short pulses of opposite polarity (each of duration $t_p = 0.01$ s) which are preceded by a step potential (of duration 0.1 s). The corresponding pulse frequency was therefore $f = 1/(2t_p) = 50$ Hz. The amplitude of the pulses was 0.05 V. The potential was incremented between successive cycles by a constant step ($\Delta E = 5$ mV), and scanned from 0.2 to -0.7 V, analogously to conventional SWV. A total of 181 such modulation cycles were applied. Within current sampling was performed separately for the step potential and for each pulse, resulting in 30 sampling points per step or pulse. These sampling windows allowed reliable determination of the forward and backward pulse currents (as an average of 3 last sampling points), from which the differential (net) signal was calculated. This modulation scheme combines features of chronoamperometry with differential-pulse and square-wave voltammetry, enabling enhanced discrimination of faradaic processes while maintaining high sensitivity and temporal resolution [55]. The net-peak current corresponding to -0.6 V was used as an analytical signal, taking into account former subtraction of the blank response.

3. Results and discussion

The preliminary experiments were designed to identify an appropriate working electrode that would meet two essential requirements. The electrode had to support well-defined electrochemical reduction of H_2O_2 and, at the same time, enable stable contact with all three phases. In accordance with our previous findings, the supporting electrolyte consisted of 1%

PAA dissolved in 0.1 M aqueous KNO_3 solution, additionally containing $2 \times 10^{-4} \text{ mol L}^{-1}$ Cu(II) ions [47, 49]. The Cu(II) ions play a crucial role in the proposed sensing mechanism by participating in the $\text{Cu}^{2+}/\text{Cu}^+$ redox chemistry and enabling the electrocatalytic processes responsible for the H_2O_2 response. With respect to the three-phase arrangement of the experimental setup, several configurations were examined, including copper and gold meshes floating on the aqueous electrolyte, gold and platinum wires immersed partly in the aqueous electrolyte, and paraffin-impregnated graphite or glassy carbon rods brought into contact with the aqueous electrolyte, as depicted in Scheme 1. Initially, the measurements were conducted in an aqueous solution using a standard three-electrode system with H_2O_2 present in the electrolyte phase in order to simplify the comparison of the electrochemical response of the tested electrodes.

Some of the tested systems were excluded at an early stage of the study. Although metallic meshes offered a favourable ratio of size-to-surface area and allowed easy formation of a three-phase junction, they exhibited poor electrochemical stability of the H_2O_2 voltammetric response. The gold wire did not provide a sufficiently stable and reproducible signal, whereas the platinum wire promoted intensive hydrogen evolution, which interfered with the detection process. Consequently, only the paraffin-impregnated graphite and the glassy carbon rods were found suitable for further investigation.

The comparative results obtained using these two electrodes when H_2O_2 is present in the liquid phase only, are presented in Figure 1.

In a typical response a direct reduction of Cu(II) ions can be observed under mildly negative applied potential, i.e. from 0 up to -0.2 V in a two-step process (not visible in Fig. 1 due to large current scale) [46, 47]. Further, the strong increase in the current commencing at about -0.4 V is related to catalytic oxygen reduction at in-situ formed copper nanoparticles on the electrode surface (solution was not deaerated). Upon introduction of the H_2O_2 a proportional increment of the voltammetric response (cf. inset in Fig. 1) in the same potential region can be observed. For these reasons from the measurements with H_2O_2 the blank response was always subtracted. Among all tested materials, the glassy carbon rod was ultimately chosen as the optimal working electrode. It demonstrated superior sensitivity toward H_2O_2 , provided a highly stable current response during repeated measurements, and generated noticeably higher analytical signal in comparison with the other materials (Fig. 1, curve b). It is worth noting that the paraffin-impregnated graphite rod had a slightly larger diameter (6 mm) than the glassy carbon (5 mm). Yet, the intrinsic surface properties and electrochemical stability of glassy carbon play a decisive role in governing the overall detection performance within the proposed

system. Its wide cathodic potential window enables reliable operation at sufficiently negative potentials required for hydrogen peroxide reduction without significant interference from solvent decomposition reactions. In parallel, its low and stable double-layer capacitance contributes to a reduced background current, thereby improving the signal-to-noise ratio, which is particularly critical for low-concentration analyte detection. Moreover, glassy carbon exhibits a chemically inert and structurally stable carbon surface that resists corrosion, surface oxidation, and progressive electrode fouling under repeated electrochemical cycling. This stability is essential for maintaining a reproducible three-phase gas–liquid–solid interface, where even minor surface reconstruction could disrupt the localized reaction zone. Taken together, these combined electrochemical and interfacial properties make glassy carbon particularly well-suited for stabilizing and isolating the analytically relevant signal in the presented detection scheme.

The next stage of the study focused on verifying the composition of the supporting electrolyte. Although our earlier investigations identified optimal electrolyte system for the electrochemical detection of H_2O_2 in the gas phase in contact with microliter volumes of the liquid phase [50], the present work employs a completely redesigned experimental configuration based on electrochemistry confined to the three-phase boundary region, utilizing a macroscopic liquid volume that cannot be saturated with dissolved H_2O_2 . Accordingly, we have compared aqueous solution (10 mL) of 0.1 M KNO_3 in the absence of polyelectrolyte, with the same solution containing either PAA or pAMPS polyelectrolytes at pH 2. In all cases, Cu(II) ions were used as an electrocatalyst.

The time required to saturate the gas phase of the measurement chamber with gaseous H_2O_2 was examined, by exposing it to H_2O_2 vapours generated from 5 mL of a 1 mM aqueous H_2O_2 solution inserted separately into a chamber (the total volume of the chamber was 150 mL) [50]. The current response was monitored over a period of 75 minutes, and the representative SW voltammograms recorded after 30 minutes are presented in Fig. 2A and B. It was found that in the presence of the polyelectrolytes, saturation of the chamber with H_2O_2 vapor was not achieved even after 75 minutes, due to the increased solubility of H_2O_2 in the liquid phase (Fig. 2C). In the case of the PAA system (Fig. 2A), the signal associated with Cu(II) reduction is poorly defined, and only an increase in the cathodic current is observed at more negative potentials. Such behaviour is consistent with the high solubility of H_2O_2 in the polyelectrolyte containing aqueous phase.

In contrast, for the 0.1 M KNO_3 system free of polyelectrolytes (Fig. 2B), the copper-related signal at about 0.05 V is clearly resolved, and the voltammetric response exhibits a more

defined structure. The introduction of H₂O₂ in the gas phase does not significantly alter the overall shape of the voltammetric curve; however, a noticeable increase in cathodic current is observed at more negative potentials, due to contribution of direct H₂O₂ electrochemical reduction.

When 0.1 M KNO₃ aqueous solution was used as the sole liquid phase, the highest signal was observed after 30 minutes, followed by stable saturation of the gas phase with H₂O₂ vapours (Fig. 2C). As the macroscopic liquid phase cannot be saturated with dissolved H₂O₂, these data imply that the response of H₂O₂ predominantly originate from its electrochemistry at the three-phase boundary region. Thus, comparing to our previous findings, the three-phase configuration enables simplification of the chemical composition of the liquid phase, yet providing reproducible and stable voltammetric signal.

Following optimization of the working electrode and liquid phase composition, quantitative measurements of gaseous H₂O₂ were performed in the thus-composed three-phase system. The gas chamber was exposed to a defined concentration of H₂O₂ for 30 min and the corresponding currents were recorded at -0.6 V using SWV. Representative voltammograms are presented in Fig. 3. In comparison with the blank signal (curve a), all subsequent voltammograms (curves b – e) exhibit proportional increase of the cathodic current with increasing H₂O₂ concentration in the gas phase, particularly in the region of more negative potentials.

In contrast, the signal associated with the Cu(II) reduction at about 0.05 V is less stable and does not correlate clearly with the gaseous H₂O₂ concentration. It is worth noting that, in the presence of H₂O₂, the electrochemical reduction of Cu(II) follows an EC' reaction scheme, in which the kinetics of the regenerative follow-up chemical step depends on the concentration of H₂O₂ [46, 47]. Considering that H₂O₂ is predominantly confined to the three-phase region, without being sufficiently dissolved in the aqueous phase, the EC' reaction can occur only at the three-phase boundary. In parallel, the conventional electrode reaction of Cu(II) reduction proceeds at the remainder of the electrode surface, which is in contact solely with the aqueous phase. Thus, the voltammetric response at approximately 0.05 V reflects two concurrent electrode mechanisms, with the Cu(II) reduction in a solution free (or with a minute amount of dissolved H₂O₂) being dominant. As a result, this signal cannot be reliably used for the indirect detection of H₂O₂ in the present three-phase experimental configuration.

Based on the observed voltammetric responses, a clear linear relationship between the current response and the gaseous H₂O₂ concentration was established in the range from 1.85×10^{-12} to 2.96×10^{-11} mol L⁻¹. Note that the assumed gaseous concentrations of H₂O₂ have been

calculated considering Henry's law [57, 58]. Within the concentration interval, the calibration plot exhibited good linearity ($R^2 = 0.998$), confirming that the proposed arrangement can be reliably used for quantitative sensing. The sensitivity of the proposed sensing system was determined to be $678.6 \mu\text{A per mmol L}^{-1}$, indicating a highly responsive electrochemical behavior toward ultra-trace concentrations of hydrogen peroxide in the gas phase. At concentrations exceeding this range, the current response continued to increase, however, the slope of the calibration curve decreased markedly, indicating the onset of a non-linear region. The decrease in calibration slope observed at higher H_2O_2 concentrations indicates a deviation from the response behaviour found at lower concentrations. Similar changes in sensitivity between different concentration intervals are frequently encountered in analytical measurements. In the present case, the phenomenon might be associated with a change in the dominant electrode mechanism. A possible explanation is that, at elevated H_2O_2 concentrations, the electrode reaction is not confined exclusively to the three-phase boundary line but extends into the adjacent solution region due to local dissolution of H_2O_2 near the three-phase reaction zone, although the exact origin of this behaviour requires further investigation. Measurements were carried out on different days under non-controlled ambient conditions, including variations in temperature and pressure, while maintaining stable and reproducible sensor performance. The limit of detection (LOD) was calculated as $1.28 \times 10^{-13} \text{ mol L}^{-1}$, while the limit of quantification (LOQ) was determined to be $4.28 \times 10^{-13} \text{ mol L}^{-1}$. The calculation was based on the standard $k\text{SD}/b$ formula, where $k = 3$ for LOD and 10 for LOQ, SD represents the standard deviation of the intercept, and b corresponds to the slope of the calibration curve [59]. Methods' precision was examined using three separate series of measurements, giving an average relative standard deviation of 3.3%, which indicates satisfactory repeatability of the analytical signals. Additional recovery calculations resulted in values between 93.4 and 103.2%, demonstrating that the system provides accurate results without systematic bias.

Following conventional SWV, advanced electroanalytical methods have been applied as electrochemical faradaic spectroscopy (EFS) [54] and differential square-wave voltammetry (DSWV) [55] to further evaluate the analytical capabilities of the three-phase system. Representative electrochemical responses obtained using SWV, EFS, and DSWV are comparatively presented in Fig. 4. The EFS measurements were performed by means of 30 potential cycles with a SW amplitude being identical as in conventional SWV, whereas the mid-potential was -0.6 V [54]. Fig. 4B depicts variation of the net, forward and backward components of the EFS response as a function of the serial number of potential cycles. The final

analytical signal was obtained by averaging the net currents from the five last cycles followed by appropriate subtraction of the blank response.

A well-defined linear dependence between the relative current response and the gaseous H_2O_2 concentration was obtained within the range of 3.7×10^{-13} to 3.7×10^{-12} mol L^{-1} (Fig. 5, curve b). The calibration plots constructed from three independent measurement series demonstrated satisfactory reproducibility across the entire concentration range, with an average relative standard deviation of 5.3%. In addition, the proposed EFS-based sensing approach exhibited a high analytical sensitivity of 6879 μA per mmol L^{-1} of gaseous H_2O_2 , substantially exceeding the sensitivity obtained using conventional SWV measurements. The LOD of gaseous H_2O_2 was determined to be 7.79×10^{-14} mol L^{-1} , while recovery experiments yielded values between 85.8 and 105.1%. These results indicate that the application of EFS allows ultrasensitive detection of H_2O_2 , while maintaining satisfactory quantitative performance. The enhanced sensitivity achieved with EFS can be attributed to the selective sampling of the faradaic component of the current and the reduction of capacitive background contributions [60].

For DSWV, the measurements were performed within the potential range from 0.2 to -0.7 V with a step potential of 5 mV. Each potential cycle consisted of a potential step followed by two pulses of opposite polarity [55]. Under these conditions, a linear analytical response was observed ranging from 3.7×10^{-14} to 3.7×10^{-13} mol L^{-1} (Fig. 5, curve c). The calibration lines obtained from three independent measurement series demonstrated very good reproducibility, with an average relative standard deviation of 1.3%, indicating excellent precision of the method. Recovery values varied between 87.6 and 104.1%, confirming satisfactory analytical accuracy. The DSWV methodology additionally provided an exceptionally high analytical sensitivity of 64.03 mA per mmol L^{-1} , markedly higher than that achieved using both conventional SWV and EFS approaches. Based on the calibration data, the limit of detection was calculated as 2.79×10^{-15} mol L^{-1} , while the corresponding limit of quantification was estimated at 9.29×10^{-15} mol L^{-1} , which to the best of our knowledge, is the lowest detection limit for the gaseous H_2O_2 reported so far (Table 1). Accordingly, both the LOD and LOQ were reduced by approximately one order of magnitude compared with the techniques discussed above.

3.1 Interferences

Additional experiments were performed to evaluate the behaviour of the sensor in the presence of selected gaseous interfering species, namely NH_3 , NO_2 , and SO_2 . Representative SW voltammograms are presented in Fig. S1 in the Supplementary Material. Due to the lack of precise control over the concentrations of interfering gases, the results should be considered qualitative. Nevertheless, the performed experiments provide useful preliminary insight into the selectivity of the proposed system. The recorded voltammograms show that the response toward H_2O_2 remains largely unchanged in the region of negative potentials, where the analytical signal was sampled. Some variations are observed in the potential region associated with copper reduction, particularly in the presence of SO_2 ; however, these effects do not significantly affect the H_2O_2 signal. The observed selectivity toward H_2O_2 arises primarily from the fact that its electrochemical reduction at the confined three-phase boundary is a kinetically favourable proton-coupled electron transfer process occurring directly at the gas–liquid–solid interface, whereas NH_3 , NO_2 , and SO_2 do not undergo comparable reduction pathways at the same interface and thus do not generate significant faradaic responses at the applied potential. Although Cu(II)-related processes may be electrochemically accessible within a broader potential range, their contribution is effectively decoupled in the present system because the analytical signal is dominated by the interfacial H_2O_2 reduction confined to the three-phase boundary, while background and non-specific contributions are accounted for via blank subtraction.

3.2 Green Chemistry

The greenness of the developed procedure was evaluated using the AGREEprep metric [67], which assesses sample preparation protocols according to criteria including sample preparation placement, use of hazardous materials, sustainability and reusability of materials, waste generation, sample size economy, sample throughput, integration and automation, energy consumption, post-sample preparation analytical configuration, and operator safety. The method fulfils several principles of green sample preparation due to its in-situ operation, which eliminates sample transport and additional handling steps. Only aqueous solutions of KNO_3 , CuSO_4 , and H_2O_2 were used, without organic solvents, derivatization reagents, or strong acids and bases, resulting in low chemical hazard and minimal reagent consumption. The reusable

measurement chamber and glassy carbon electrode further reduce material usage, while waste generation is limited to small volumes of aqueous solutions.

The procedure involves a small number of manual steps and requires only a single electrochemical workstation, leading to relatively low energy consumption. The use of voltammetric techniques as the final determination step additionally supports the green character of the method due to low reagent consumption and reduced environmental impact. According to the AGREEprep evaluation (Fig. S2), the developed protocol achieved a greenness score of 0.66, indicating favourable environmental performance and good compliance with the principles of green analytical chemistry.

4. Conclusions

The analytical figures of merit obtained in this work confirm that H₂O₂ can be reliably detected and quantified at the electrochemical three-phase interface using extremely simple experimental configuration and chemical composition of the aqueous phase (i.e., aqueous solution containing only KNO₃ and Cu(II) ions). The proposed system enables direct interaction of gaseous H₂O₂ with the working electrode and provides reliable measurements at trace levels of the analyte. Overall, the integration of optimized electrode selection, appropriate supporting electrolyte, rationally designed three-phase interface, combined with advanced voltammetric methods, has led to enhanced sensitivity and improved analytical performance in comparison with our previous studies [47, 49], confirming the practical usefulness of the developed platform for monitoring H₂O₂ in the gas phase.

Nevertheless, several limitations of the current approach should also be mentioned. In particular, both electrochemical faradaic spectroscopy and differential square-wave voltammetry required the development of particular potential modulation and signal-processing procedures, since these techniques are not yet commonly implemented in standard commercial electrochemical software. Furthermore, the present study was performed under laboratory conditions using a proof-of-concept experimental configuration; therefore, further investigations involving long-term stability, quantitatively controlled interference studies, and validation using real gaseous samples will be necessary in future work.

Acknowledgements

This research was funded in whole or in part by National Science Center, Poland 2020/39/I/ST4/01854.

Competing Interest Statement

The authors declare no conflict of interest.

Data availability

Data available upon reasonable request from corresponding authors.

Authors contribution

Conceptualization DG, VM; Data curation BB; Formal analysis BB; Funding acquisition VM; Investigation BB, DG; Methodology DG, VM; Project administration DG; Supervision DG, VM; Validation DG; Visualization BB, NU; Writing - original draft BB, DG, VM; Writing - review & editing BB, DG, NU, VM.

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Table and Table Caption

Table 1. Comparison of electrochemical detection and quantification limits reported in the literature.

Electrochemical sensor/Method	Phase	Linear range (mol L ⁻¹)	LOD (mol L ⁻¹)	Ref
PB-SPE/SWV	Liquid	$1 \times 10^{-5} - 1 \times 10^{-3}$	2.3×10^{-6}	[49]
PB-GCE/Amperometry	Liquid	$5 \times 10^{-7} - 1 \times 10^{-3}$	3.0×10^{-7}	[61]
PBNCs/rGO-GCE/Amperometry	Liquid	$5 \times 10^{-8} - 1.2 \times 10^{-4}$	4.5×10^{-8}	[62]
PB-SPE/Amperometry	Liquid	$4 \times 10^{-7} - 1 \times 10^{-4}$	4.0×10^{-7}	[63]
GCE/SWV	Gas	$1 \times 10^{-4} - 1 \times 10^{-3}$ $1 \times 10^{-3} - 7 \times 10^{-3}$	1.2×10^{-4}	[47]
pAMPS-PB-SPE/SWV	Gas	$3.7 \times 10^{-11} - 3.7 \times 10^{-10}$	8.7×10^{-12}	[50]
Ti ₃ C ₂ T _x MXene/FCN-SPCE/CV	Gas	$1.5 \times 10^{-8} - 8.8 \times 10^{-7}$	1.2×10^{-10}	[64]
PAA-SPE/CV	Gas	$4.4 \times 10^{-7} - 3.6 \times 10^{-6}$	5.9×10^{-8}	[65]
NiCo ₂ Se ₄ /GC/SWV	Gas	$1.22 \times 10^{-11} - 6.1 \times 10^{-11}$	---	[66]
TPh-GC rod/SWV	Gas	$1.85 \times 10^{-12} - 2.96 \times 10^{-11}$	1.28×10^{-13}	This work
TPh-GC rod/EFS	Gas	$3.7 \times 10^{-13} - 3.7 \times 10^{-12}$	7.79×10^{-14}	This work
TPh-GC rod/DSWV	Gas	$3.7 \times 10^{-14} - 3.7 \times 10^{-13}$	2.79×10^{-15}	This work

PBNCs Prussian blue nanocubes, rGO reduced graphene oxide, SPE screen-printed electrode, TPh three-phase system

Scheme and Figure Captions

Scheme 1. Schematic representation of a three-phase analysis system.

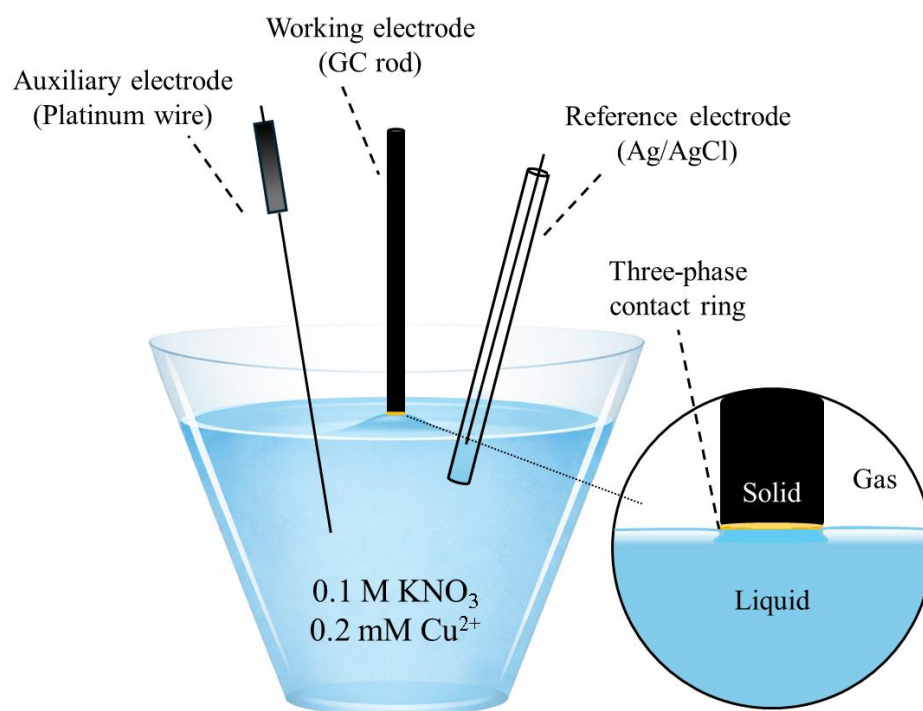
Fig. 1. SW voltammetric response of $1 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ aqueous solution dissolved in 1% PAA and 0.1 M KNO_3 with addition of $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ using paraffin-impregnated graphite (a) and glassy carbon rod (b) as working electrodes in a three-phase electrochemical cell configuration as depicted in Scheme 1. Inset: corresponding current sampled at -0.6 V as a function of H_2O_2 concentration after subtraction of the blank response. SW parameters: frequency 8 Hz, amplitude 0.050 V, and step potential -0.005 V .

Fig. 2. Square-wave voltammograms recorded in the three-phase system for different supporting electrolytes containing $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$: (A) 1% PAA in 0.1 M KNO_3 and (B) only 0.1 M KNO_3 ; curves: (a) blank and (b) after exposure to gaseous H_2O_2 . (C) Relative current response as a function of saturation time after exposing 1 mM H_2O_2 introduced into 5 mL of water in a separate vessel within a sealed 150 mL chamber, for different supporting electrolytes: (a) 0.1 M KNO_3 , (b) 1% PAA, and (c) 1% pAMPS (both (b) and (c) in 0.1 M KNO_3). SWV parameters: frequency 8 Hz, amplitude 0.050 V, step potential -0.005 V .

Fig. 3 SW voltammograms recorded at a GC rod in the three-phase system for selected H_2O_2 concentrations with a supporting electrolyte consisting of 0.1 M KNO_3 and $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$. Curves: (a) blank, (b) 1.85×10^{-12} , (c) 3.7×10^{-12} , (d) 1.85×10^{-11} , (e) $2.59 \times 10^{-11} \text{ mol L}^{-1}$ of H_2O_2 in the gas phase. SW parameters: frequency 8 Hz, SW amplitude 0.05 V, step potential -0.005 V .

Fig. 4. Comparison of electrochemical responses obtained using different voltammetric techniques in the three-phase gas–liquid–solid system: (A) SWV, (B) electrochemical faradaic spectroscopy, and (C) differential square-wave voltammetry. Measurements were performed in 0.1 M KNO₃ supporting electrolyte containing 2×10^{-4} mol L⁻¹ Cu(II) ions in the presence of gaseous H₂O₂ comprising (a) forward, (b) backward, (c) net and (d) potential step responses

Fig. 5 Comparison of calibration curves obtained for gaseous H₂O₂ using three electrochemical techniques: (a) SWV, (b) EFS, and (c) DSWV at three-phase electrochemical interface experimental conditions.



Scheme 1.

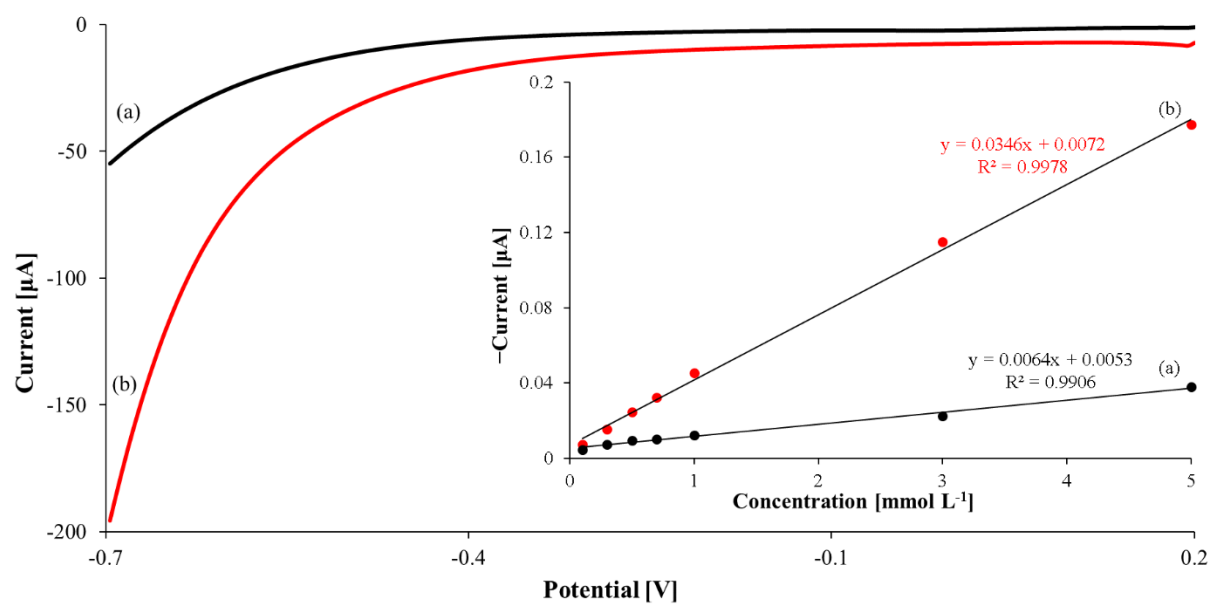


Fig. 1

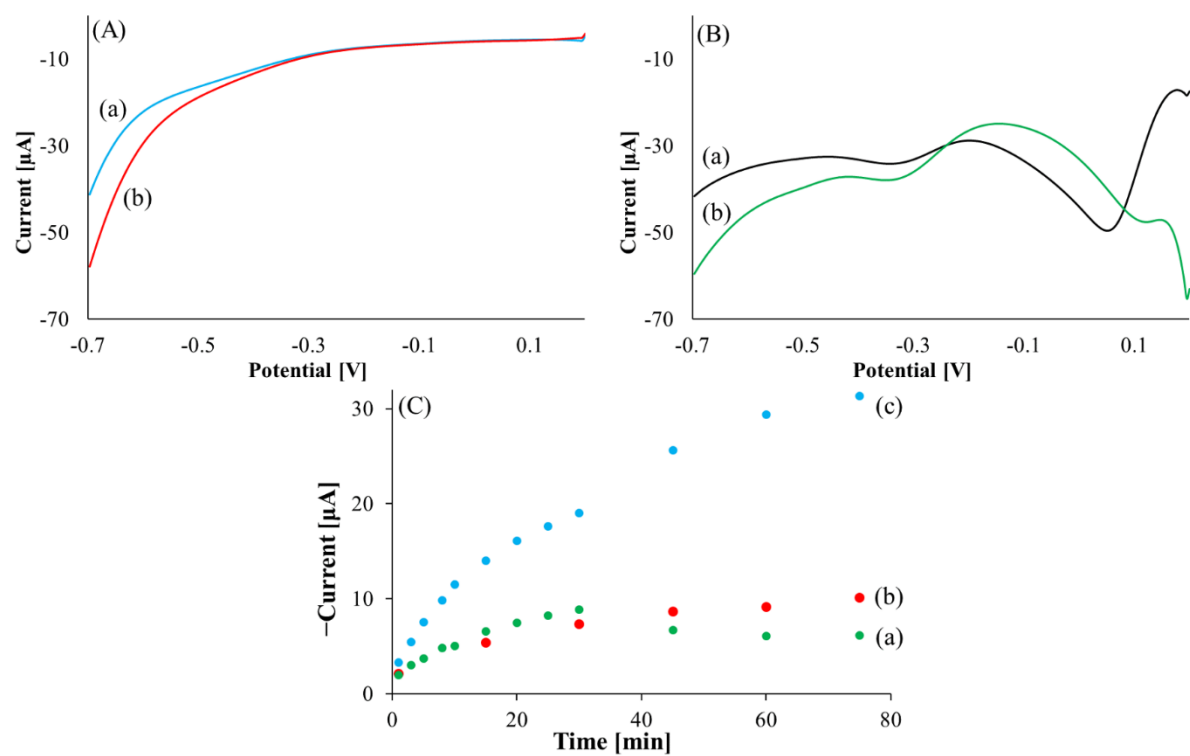


Fig. 2

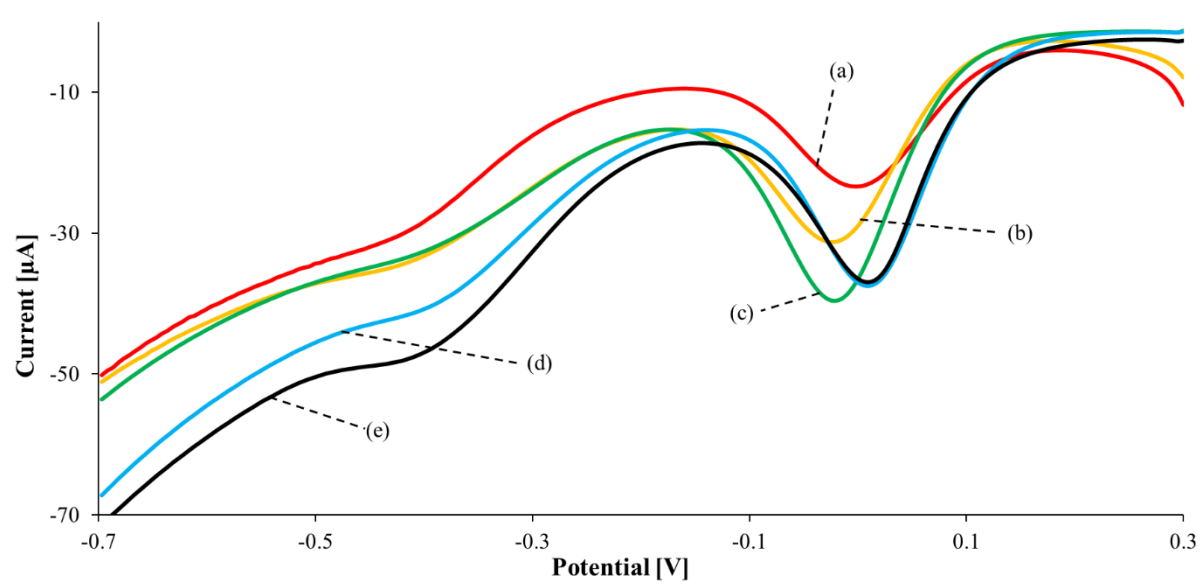


Fig. 3

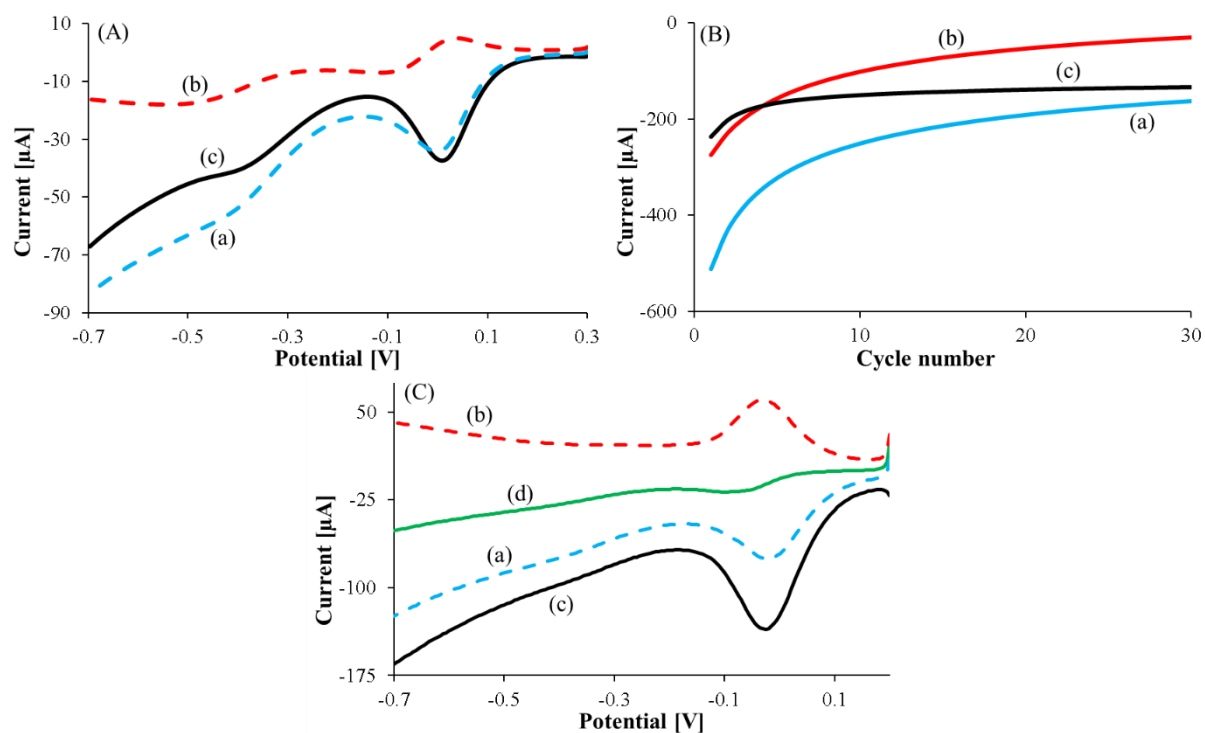


Fig. 4

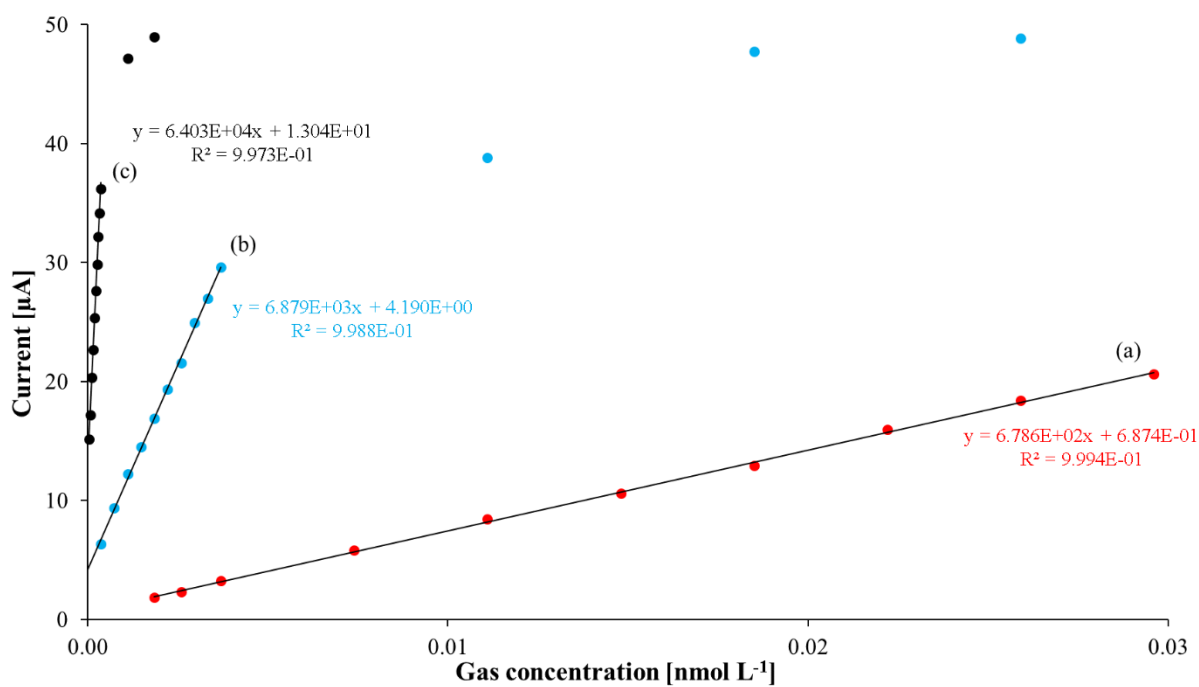
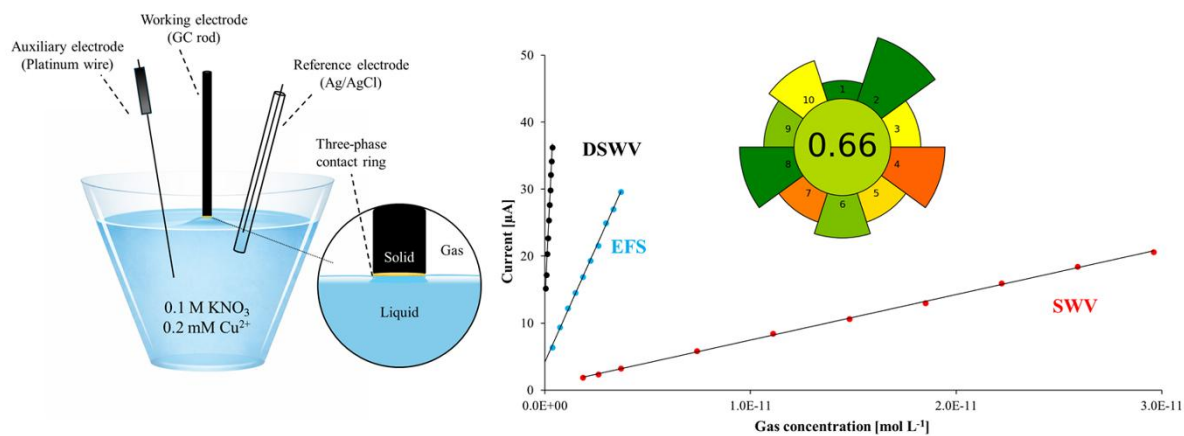


Fig. 5



Graphical abstract

Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface

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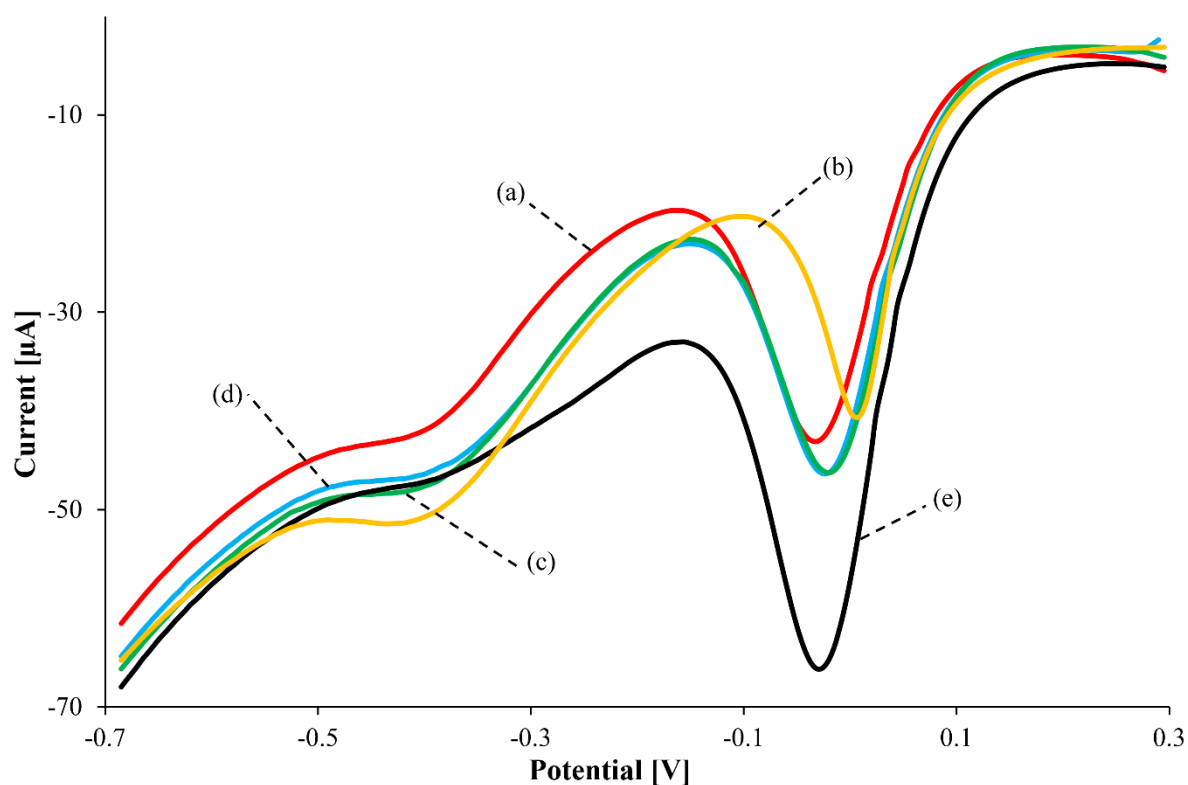


Fig. S1 Square-wave voltammograms recorded with a GC rod in the three-phase system in a 0.1 M KNO₃ supporting electrolyte with added 2×10^{-4} mol L⁻¹ Cu²⁺ and H₂O₂ (3.7×10^{-12} mol L⁻¹) for individual interfering substances: (a) supporting electrolyte; KNO₃+Cu²⁺ (H₂O₂ absent), (b) blank, (c) NH₃, (d) NO₂, (e) SO₂. Experimental conditions: amplitude 50 mV, frequency 8 Hz, step potential -0.005 V.

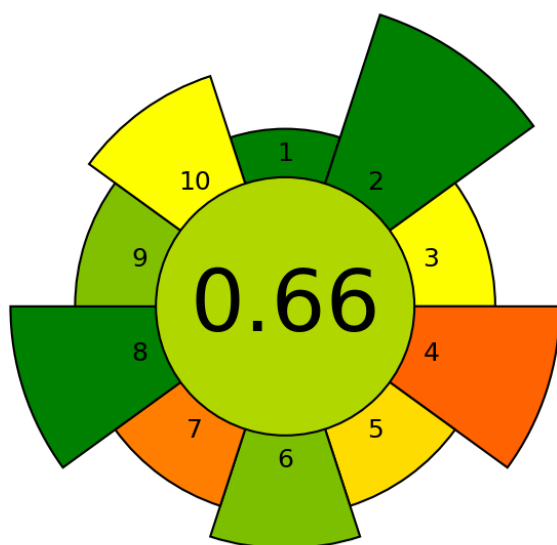


Fig. S2 Results of the greenness assessment of the developed measurement procedure using the AGREeprep tool, criteria: (1) sample preparation placement, (2) hazardous materials, (3) sustainability, renewability, and reusability of materials, (4) waste, (5) size economy of the sample, (6) sample throughput, (7) integration and automation, (8) energy consumption, (9) post-sample preparation configuration for analysis, (10) operator's safety.

Łódź, 08.06.2026 r.

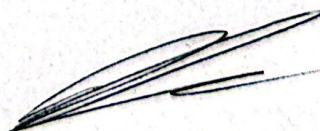
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Oświadczenie współautora

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- N. Ullah, D. Guziejewski, B. Barton, V. Mirceski, Electrocatalytic reduction of hydrogen peroxide in solution in the presence of polyacrylic acid and copper ions: Application for gaseous hydrogen peroxide detection, Journal of Electroanalytical Chemistry, 951 (2023) 117918.
- B. Barton, N. Ullah, D. Guziejewski, P. Krzyczmonik, V. Jovanovski, V. Mirceski, Detection of gaseous hydrogen peroxide using polyacrylic acid–copper(II) catalytic system at carbon-based screen-printed electrodes, Ionics, 31 (2025) 12245–12256.
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- B. Barton, N. Ullah, V. Mirceski, D. Guziejewski Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface; Microchemical Journal, (2025) submitted.

współtworzeniu ogólnej koncepcji oraz planu badań, sprawowaniu nadzoru merytorycznego nad realizacją prac badawczych, udziale w walidacji uzyskanych wyników, a także współudziale w przygotowaniu oraz redakcji manuskryptów przeznaczonych do publikacji. Swoj wkład w przygotowanie każdej z nich oceniam na 10%.



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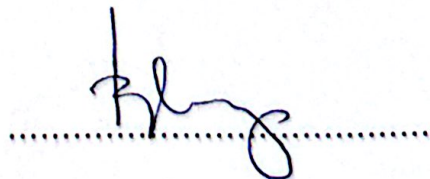
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Declaration

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co-participation in the development of the research concept and methodological framework, scientific supervision of the conducted studies, participation in the validation and interpretation of the obtained results, acquisition of research funding, and co-participation in the preparation, review, and editing of the manuscripts. I estimate my contribution to the preparation of each publication at 10%.





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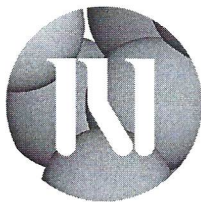
co-participation in the development of the experimental methodology, experimental investigations, data curation and formal analysis, as well as co-participation in the preparation, review, and editing of the manuscript. I estimate my contribution at 50%.

For publications:

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- B. Barton, N. Ullah, V. Mirceski, D. Guziejewski Detection of Gaseous Hydrogen Peroxide at a Three-Phase Electrochemical Interface; Microchemical Journal, (2025) submitted

my contribution consisted of participation in experimental investigations, data visualization, contribution to the review, and editing of the manuscripts. I estimate my contribution to the preparation of each publication at 5%.

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consisted of participation in the results discussion and contribution to the review and editing of the manuscripts. I estimate my contribution to the preparation of each publication at 5 %.

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