Mechanism of the electrochemical response of gallic acid at a porous electrode: The (ir)reversibility paradox

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Introduction

Although the electrochemistry of the gallic acid (GA) is commonly described as electrochemically irreversible, we show that the voltammetric response can be varied from electrochemically irreversible to reversible depending on experimental conditions. Building on our previous results regarding the diffusion domains in the porous SWCNTs layer [1], this work focuses on explaining the mechanism of the voltammetric behavior of the GA at SWCNTs-modified glassy carbon electrode (GCE). Under certain experimental conditions, counter-intuitive behavior can be observed, where a significantly improved voltammetric signal is obtained with low supporting electrolyte concentration. Detailed analysis of results from cyclic voltammetry (CV), reverse pulse voltammetry (RPV), and double potential step chronoamperometry (DPSCA) reveals that the electrochemical behavior is governed by a complex interplay between different mass transport phenomena occurring within the porous SWCNTs layer, with emphasis on those near the GCE. Pristine SWCNTs, contrary to the widely accepted view, do not contribute to the electrochemical response through their "inherent electrocatalytic?!" properties, but through their role in mass transport and "sponge" (reservoir) effect.

Keywords: gallic acid, porous, mass transport, (ir)reversibility paradox, electrochemistry

[1] J. Dugeč, I. Škugor Rončević, *Int. J. Mol. Sci.* 26 (2025) 8262.

Methods

SOLUTIONS:

- **Support:** Britton-Robinson buffers (0.001 M, 0.01 M and 0.1 M).
- **Redox species**: Daily prepared water solution of the gallic acid..

ELECTROCHEMICAL SYSTEM:

- **Electrodes:** Ag/AgCl reference electrode, Pt auxiliary electrode and GCE (K type, 2 mm Sigradur) and GCE modified SWCNTs

ELECTRODE MODIFICATION:

- GCE modified with 1,5 µL (*SWCNT*) and 3 µL of SWCNT (*2SWCNT*) suspension c = 0.5 mg mL^{-1} by drop-casting

MORPHOLOGY:

- Optical 3D profilometry (Filmetrics)
- SEM

ELECTROCHEMISTRY on Autolab PGSTAT 302N potentiostat**:**

- **CV**: E= –0.10 to +0.60 V vs. Ag/AgCl; v= 12–400 mV s^{-1}
- **DPSCA:** E_{pulse} = +0.50/+0.03 V; t_{pulse} = 10 s
- **RPV:** E_{base} = +0.60 V; v = 50 mV s^{-1}; τ = 0.5 s; t_{pulse} = 0.4 s

***SUMARUM*:**

- 3 electrodes (**GCE, SWCNT, 2SWCNT**)
- 3 support ionic strengths (**0.001 M, 0.01 M, 0.1 M**)
- 3 concentrations of the GA (5×10^{-5} M, **1×10^{-4} M,** 5×10^{-4} M) + **Physical accumulation/PhA (1 min in 5×10^{-4} M GA)** + **Chronoamperometric accumulation/CAA (exhausting electrolysis at +0.03 V during 10 s)**

* **bold –** partially presented here

Results (MORPHOLOGY)

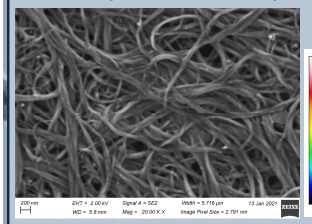

Fig. 1. SEM of the drop-casted SWCNTs layer on a glassy carbon electrode (GCE).

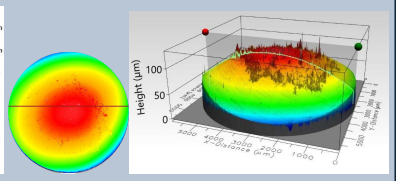

Fig. 2. Optical 3D profilometry of the drop-casted SWCNTs layer on a glassy carbon electrode (GCE).

Results (RPV)

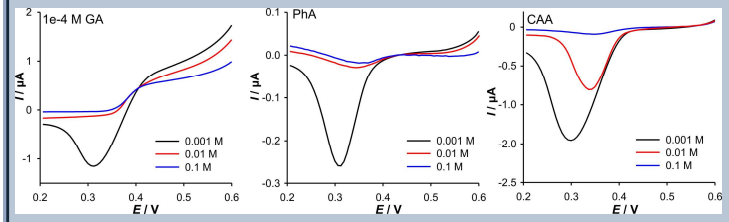

Fig.11. RPV recorded at SWCNT in different buffers..

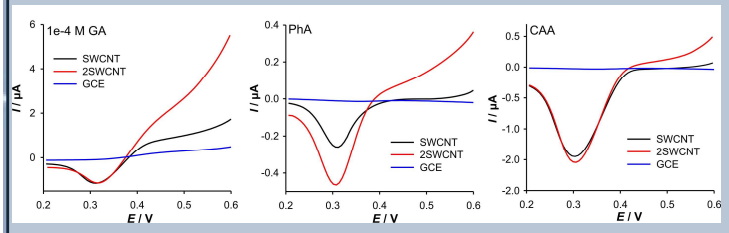

Fig.12. RPV recorded at different electrodes in 0.001 M B-R buffer.

Results (CV)

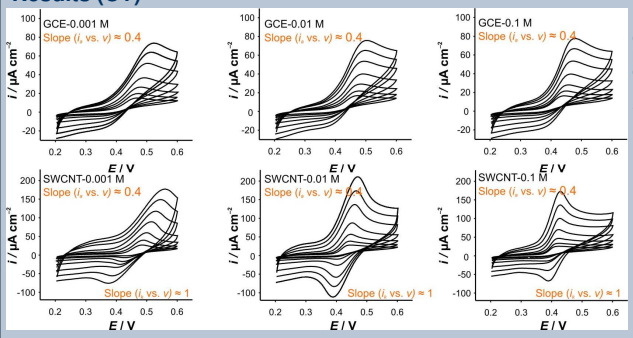

Fig. 3. CV recorded at a different electrodes in the presence of 100 µM GA in different concentrations of B-R buffers and at different scan rates (12-400 mV s^{-1}).

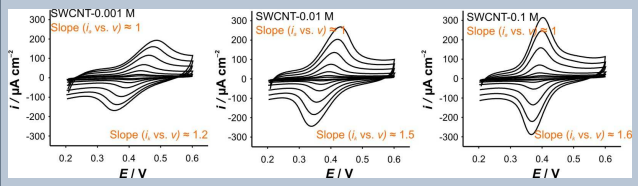

Fig. 4. CV recorded after chronoamperometric accumulation (CA) of GA on SWCNTs/GCE in different concentrations of B-R buffers and at different scan rates (12-400 mV s^{-1}).

Results (DPSCA)

SWCNT ELECTRODE.

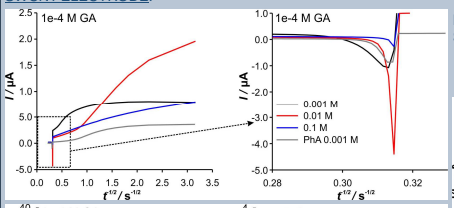

Fig. 5. Dependence of the current on $t^{-1/2}$, for the SWCNTs electrode, in different concentrations of B-R.

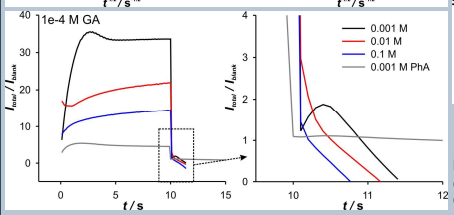

Fig. 6. Dependence of I_{total}/I_{blank} vs. t, for the SWCNTs electrode, in different concentrations of B-R. Data extracted from the Fig. 4.

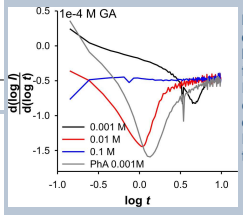

Fig.7. d(log(I))/d(log(t)) vs. log(t) dependencies for anodic part of the DPSCA, for SWCNTs electrode in different concentrations of B-R. Data extracted from the Fig. 5.

DIFFERENT ELECTRODES.

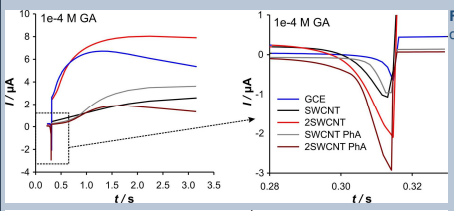

Fig. 8 . Dependence of the current on $t^{-1/2}$, for the different electrodes in 0.001 M B-R buffer including PhA.

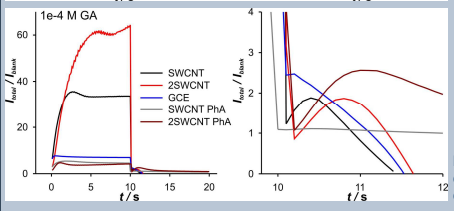

Fig. 9. Dependence of I_{total}/I_{blank} vs. t, for the different electrodes in 0.001 M B-R buffer including PhA. Data extracted from the Fig. 8.

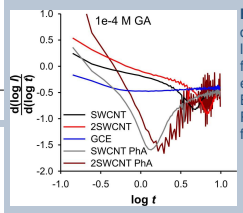

Fig.10. d(log(I))/d(log(t)) vs. log(t) dependencies for the different electrodes in 0.001 M B-R buffer including PhA. Data extracted from the Fig. 8.

Discussion

- Recorded CVs indicate a diffusion-controlled anodic reaction and an adsorption mechanism for the cathodic reaction. However, they do not show where the reaction takes place.
- DPSCA measurements reveal, in the anodic part of the DPSCA, different regions that can be attributed to diffusion phenomena through the porous SWCNT layer. These phenomena become more pronounced with increasing SWCNT layer thickness. The cathodic part of the DPSCA reveals that the cathodic reaction is influenced by the concurrent anodic reaction (Figure 6). With increasing B-R buffer concentration, reversibility causes a lack of measurable current. Slopes extracted from the DPSCA clearly indicate, in the anodic part, a strong influence of thin-layer electrochemistry.
- RPV at different electrodes indicates that charge transfer is independent of the SWCNT layer thickness. This leads to the conclusion that electron transfer takes place only at the GCE surface. The influence of reversibility (e.g. the presence of GA in the layer) is clearly revealed in the physical accumulation measurements.

Conclusion

- The counter-intuitive observation (improved voltammetric response at low supporting electrolyte concentration) on SWCNT-modified electrodes was analysed in detail, and it was concluded that the electrochemical behaviour is controlled by the interplay between different diffusion (mass-transport) phenomena in the porous SWCNT layer in the vicinity of the GCE.
- DPSCA results revealed that mass-transport effects (together with electrode kinetics) play a key role in the generation of the electrochemical signal. These mass-transport effects are hampered diffusion through the porous SWCNT layer in combination with thin-layer effects.
- RPV results revealed that the reaction takes place at the GCE electrode; thus SWCNTs are electrochemically inert and act as a reservoir ("sponge") and as a barrier for the electrochemically generated species diffusing towards the solution.
- By distinguishing the processes that occur in solution from those in the porous layer, unexpected slopes (around 1.5) of log u–log i, together with unusual variation of the log u–Epeak dependence (not shown), were attributed to the impact of electrochemical reversibility caused by mass-transfer effects in the vicinity of the GCE.
- Based on mechanistic insight into the electrochemical processes that occur in the porous SWCNT layer, the anodic branch of the cyclic voltammograms is divided into different regions according to the dominant processes that govern the electrochemical response (see Graphical Abstract).