

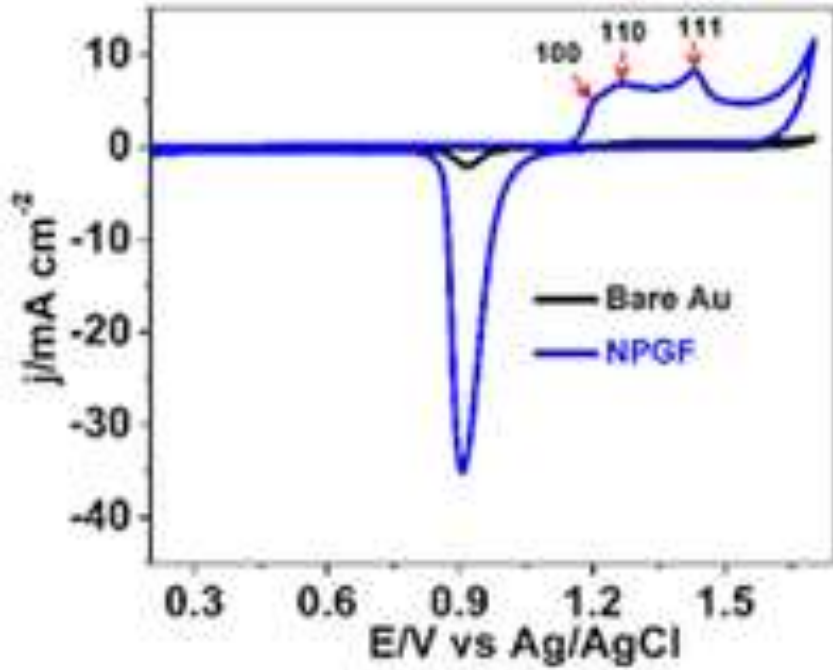
# Voltammetry Beyond the Peaks: Experimental Pitfalls, Mechanistic Ambiguities and Theoretical Challenges

*Pavle Apostoloski, Rubin Gulaboski*

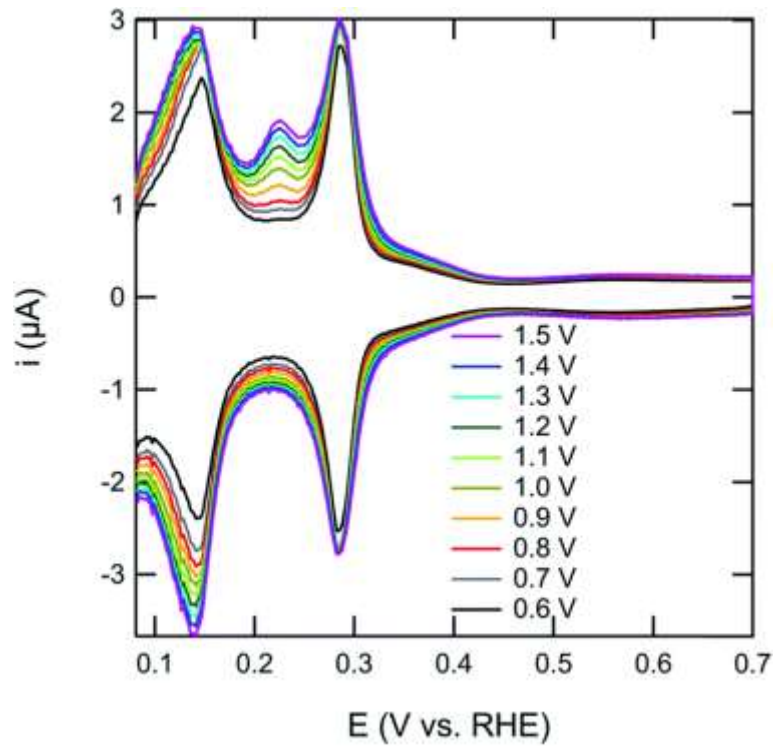
Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

## Abstract

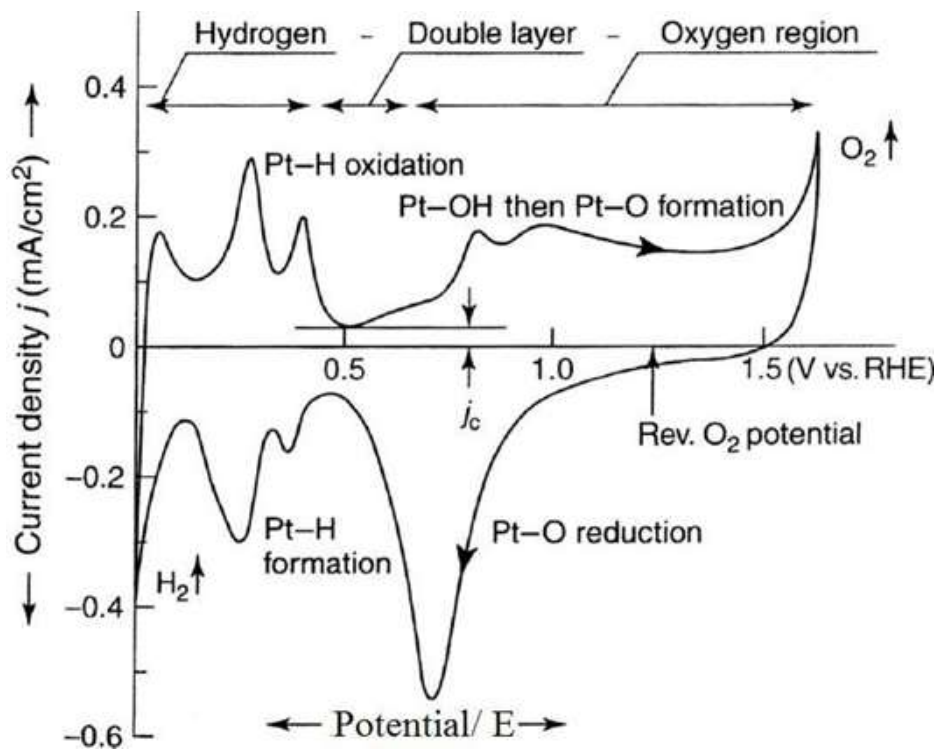
Voltammetric techniques are widely applied for mechanistic investigations and analytical determinations because the recorded current–potential responses often provide valuable information about the kinetics and thermodynamics of redox processes. However, interpretation of voltammetric data frequently extends far beyond the simple analysis of peak shapes and positions. In practical experiments, the electrode material itself can introduce additional signals and artifacts that complicate the mechanistic interpretation of the voltammograms. For instance, gold electrodes typically exhibit two prominent peaks originating from the intrinsic redox activity of surface gold oxides, which may overlap with signals of the investigated redox systems. Platinum electrodes, on the other hand, commonly display characteristic features associated with the proton reduction and hydrogen evolution reaction ( $H^+/H_2$ ), often appearing as additional peaks in the voltammetric response. Carbon-based electrodes, including various graphite materials, are prone to adsorption phenomena involving organic compounds, which can significantly distort peak currents and shapes unless the electrode surface is regularly cleaned and regenerated. Furthermore, screen-printed electrodes, although highly convenient for portable and disposable sensing applications, are generally optimized for single-use measurements, limiting their reproducibility in mechanistic electrochemical studies. These practical limitations highlight the experimental pitfalls and mechanistic ambiguities inherent to voltammetric measurements and illustrate the ongoing theoretical and methodological challenges in identifying a truly universal electrode material for voltammetric investigations. We give here some practical examples of the undesired redox activities going on when working voltammetry with these electrodes.



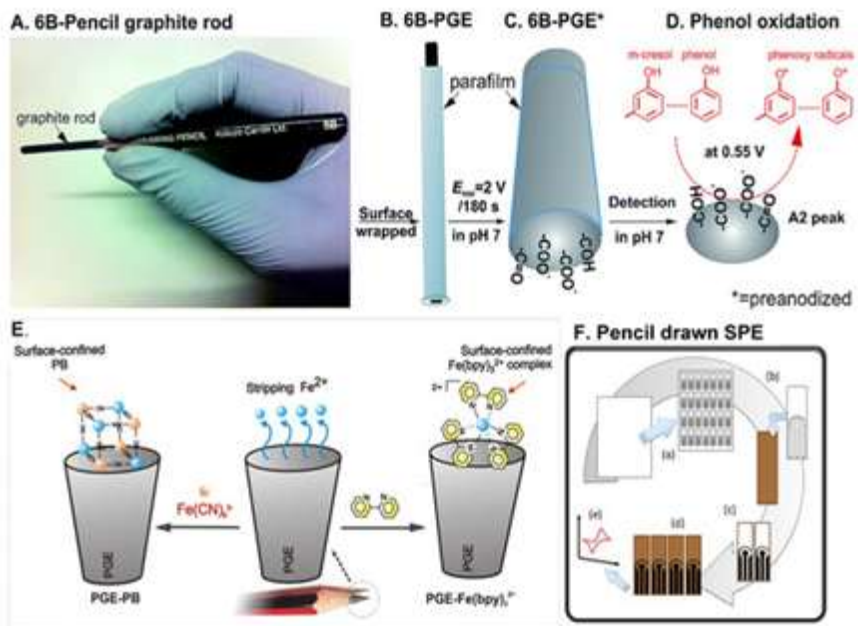
Features of Au-electrode in Cyclic Voltammetry



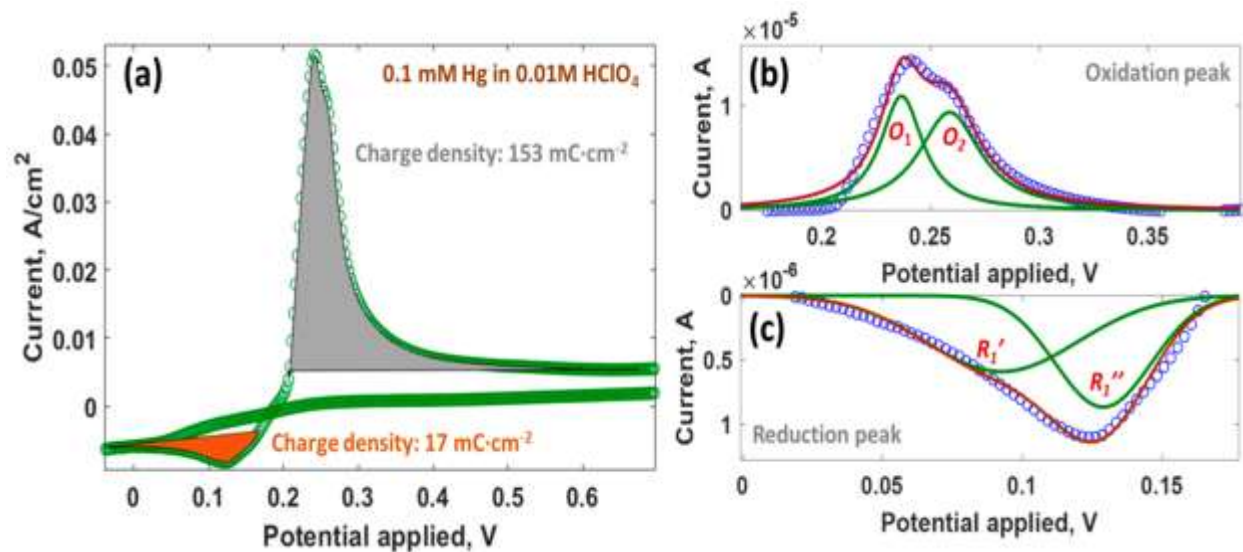
Cyclic voltammetry of Hydrogen adsorption and redox activity at Pt electrode



All processes going on at Pt electrode



Graphite electrodes prone for adsorption phenomena



Features of Mercury Electrode in Voltammetry

## REFERENCES

1. R. Gulaboski, *Journal of Solid State Electrochemistry* 24 (2020) 2081-2081
2. R. Gulaboski, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garau, V. Lippolis, A. F. Silva, *Journal of Physical Chemistry C* 112 (2008) 153-161
3. R. Gulaboski, V. Mirceski, M. Lovric, I. Bogeski, *Electrochemistry Communications* 7 (2005) 515-522.
4. R Gulaboski, V Mirceski, *Macedonian Journal of Chemistry and Chemical Engineering* 39 (2020) 153-166
5. V. Mirceski, R. Gulaboski, *Macedonian Journal of Chemistry and Chemical Engineering* 33 (2014), 1-12
6. V. Mirceski, R. Gulaboski, *Journal of Solid State Electrochemistry* 7 (2003) 157-165
7. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, *Electroanalysis* 31 (2019) 2488-2506

8. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, *Electroanalysis* 16 (2004) 832-842
9. R. Gulaboski, C.M. Pereira, M.N.D.S Cordeiro, I. Bogeski, F. Silva, *Journal of Solid State Electrochemistry* 9 (2005) 469-474
10. B. Sefer, R. Gulaboski, V. Mirceski, *Journal of Solid State Electrochemistry* 16 (2012) 2373-2381.
11. P. Kokoskarova, Rubin Gulaboski, *Electroanalysis* 32 (2020) 333-344.  
<https://doi.org/10.1002/elan.201900491>
12. R. Gulaboski, C. M. Pereira, *Electroanalytical Techniques and Instrumentation in Food Analysis; in Handbook of Food Analysis Instruments* (2008) 379-402.
13. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, *Journal of Physical Chemistry B* 110 (2006) 12530-12538.
14. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, *Analytical Chemistry* 91 (2019) 14904-14910.
15. V. Mirceski, R. Gulaboski, F. Scholz, *Journal of Electroanalytical Chemistry* 566 (2004) 351-360.
16. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, J. *Phys. Chem. C* 112 (2008) 2428-2435
17. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, *Electroanalysis* 16 (2004) 832-842
18. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, *Cell Calcium* 43 (2008) 615-621
19. R. Gulaboski, V. Mirceski, F. Scholz, *Amino Acids* 24 (2003) 149-154
20. V. Mirceski, R. Gulaboski, *Croatica Chemica Acta* 76 (2003) 37-48.
21. F. Scholz, R. Gulaboski, *Faraday Discussions* 129 (2005) 169-177.

22. R. Gulaboski, K. Caban, Z. Stojek, F. Scholz, *Electrochemistry Communications* 6 (2004) 215-218.
23. V. Mirceski, R. Gulaboski, *Journal of Physical Chemistry B*, 110 (2006) 2812-2820.
24. V. Mirceski, R. Gulaboski, B. Jordanoski, S. Komorsky-Lovric, *Journal of Electroanalytical Chemistry*, 490 (2000) 37-47.
25. R. Gulaboski, *Macedonian Journal of Chemistry and Chemical Engineering* 41 (2022) 151-162
26. R. Gulaboski, P. Kokoskarova, S. Petkovska, *Analytical&Bioanalytical Electrochemistry*, 12 (2020) 345-364.
27. V. Mirčeski, R. Gulaboski, F. Scholz, *Electrochemistry Communications* 4 (2002) 814-819
28. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S Cordeiro, *Molecular Physics* 104 (2006) 3627-3634.
29. R. Gulaboski, V. Mirceski, M. Lovric, *Macedonian Journal of Chemistry and Chemical Engineering* 40 (2021) 1-9.
30. R. Gulaboski, P. Kokoskarova, S. Risafova, *J. Electroanal. Chem.* 868 (2020) 114189.
31. R. Gulaboski, V. Mirceski, *Journal of Solid State Electrochemistry* 28 (2024) 1121-1130.
32. V. Mirceski, B. Mitrova, V. Ivanovski, N. Mitreska, A. Aleksovska, R. Gulaboski, *Journal of Solid State Electrochemistry* 19 (2015) 2331-2342.
33. I. Spirevska, L. Soptrajanova, R. Gulaboski, *Analytical Letters* 33 (2000) 919-928.
34. R. Gulaboski, B. Jordanoski, *Bulletin of Chemists and Technologist of Macedonia* 19 (2000) 177-181
35. R. Gulaboski, M. Lovrić, V. Mirčeski, I. Bogeski, M. Hoth, *Biophysical Chemistry* 137 (2008) 49-55.
36. R. Gulaboski, V. Mirčeski, S. Mitrev, *Food Chemistry*, 138 (2013) 116-121.

37. R. Gulaboski, V. Mirčeski, M. Lovrić, *Journal of Solid State Electrochemistry* 23 (2019) 2493-2506
38. V. Mirceski, R. Gulaboski, F. Scholz, *Electrochemistry Communications* 4 (2019) 814-819.
39. Rubin Gulaboski, V. Mirceski, *Journal of Solid State Electrochemistry* 28 (2024) 1121-1130.
40. R Gulaboski, F Borges, CM Pereira, M Cordeiro, J Garrido, AF Silva, *Combinatorial chemistry & high throughput screening* 10 (2007), 514-526