EDUCATIONAL VOLTAMMETRY: PART 6: Cyclic Voltammetry of Metal Alloys Dissolution Facilitated by a Homogeneous Follow Up Chemical Reaction

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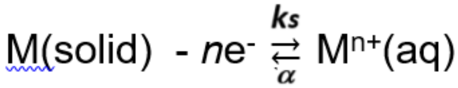
Abstract

This work presents a theoretical analysis of cyclic voltammetry (CV) for electrode processes involving the dissolution of metal alloys coupled with a homogeneous follow-up chemical reaction in solution (see the reaction scheme). The model describes a modified EC-type mechanism, where the initial electron transfer from the metallic surface to the electrolyte generates a transient species that undergoes a subsequent homogeneous reaction, influencing both the anodic and cathodic current responses. Analytical and numerical simulations were employed to examine the effect of kinetic parameters, such as the chemical rate constant, equilibrium constant, and diffusion coefficients, on the shape and position of voltammetric peaks. Particular emphasis is placed on the diagnostic criteria that distinguish simple electrochemical dissolution from dissolution–reaction sequences, including peak asymmetry, hysteresis behavior, and potential-dependent current amplification. The theoretical framework provides fundamental insight into coupling phenomena relevant to alloy corrosion, passivation, and electrocatalytic dissolution processes.



$$\mathrm{M(solid)}\ -\ ne^{-} \underset{\alpha}{\overset{ks}{\rightleftarrows}} \mathrm{M^{n+}(aq)}$$

$$\mathrm{M^{n+}(aq) + Y = MY_{(aq)}}$$

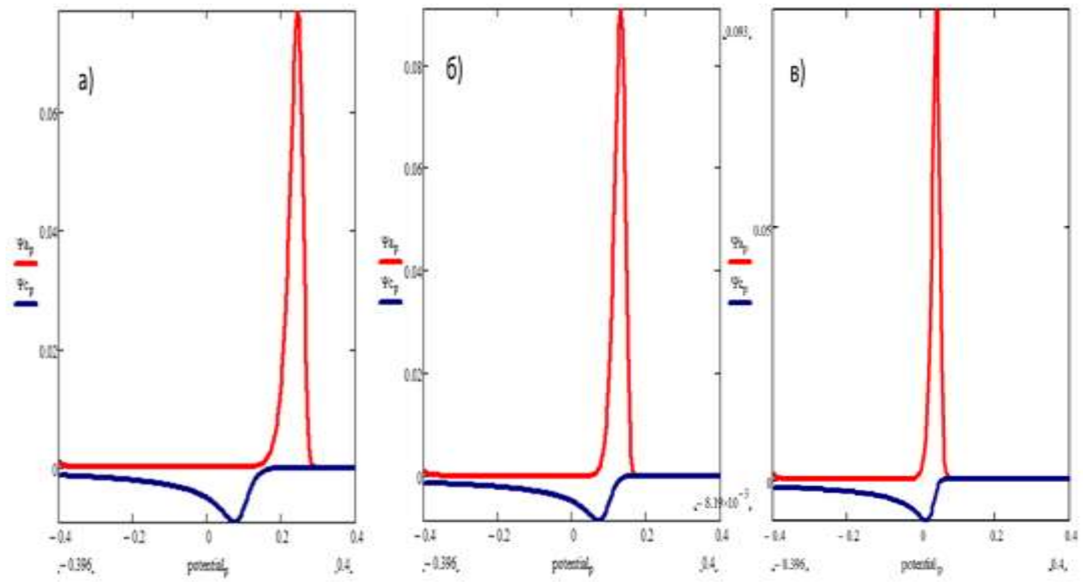


Figure 1. $M(solid) - ne^- \rightleftarrows M^{n+}(aq)$. This is a reference model of "spontaneous" alloy decay. Voltammograms are calculated ad d*E* = 2 mV $\alpha = 0.5$ scan rate od 50 mV/s. Voltammograms feature the effect of the dimensionless kinetic parameter (K) that was set to : 0.01 (а); 0.1 (б) and 1 (в).

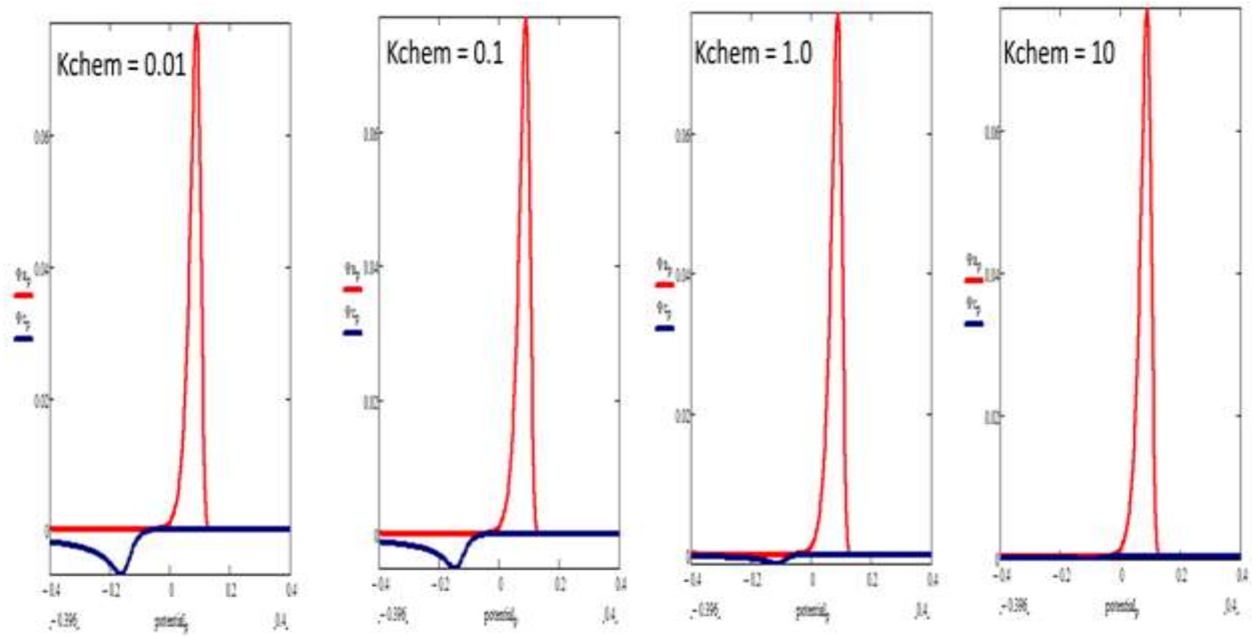


Figure 2. Voltammograms of the "facilitated" decay of metal alloy ($M(solid) - ne^- \rightleftarrows M^{n+}(aq)$.) showcasing the effect of concentration of the ligand "Y" via the magnitude of the chemical parameter $\boldsymbol{K}_{\mathbf{chem}}$.

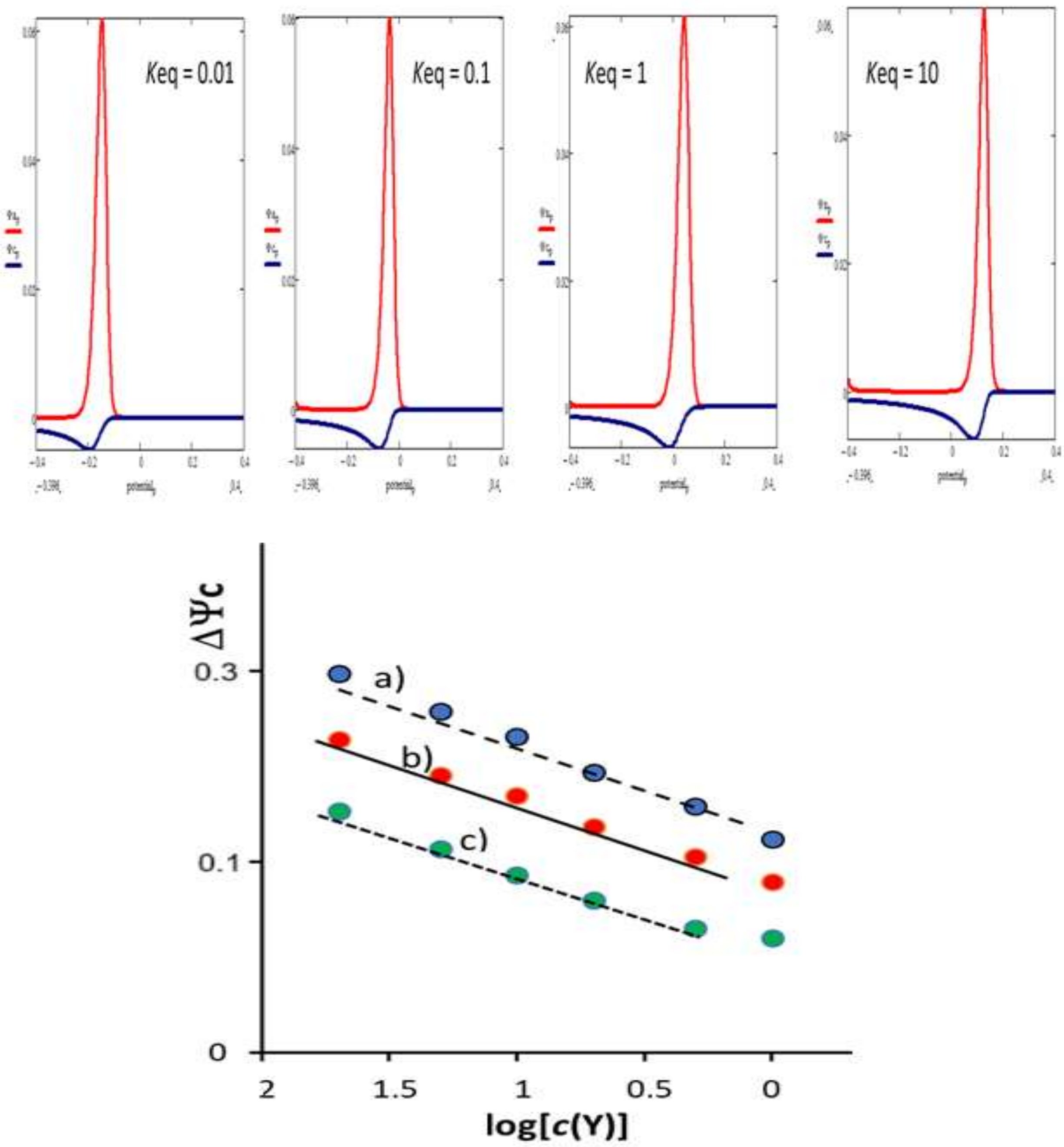


Figure 3. a) Effect of the equilibrium constant of the follow up chemical reaction to the features of calculated cyclic voltammograms of the mechanism considered in this work. b) Effect of “Y” concentration to the mid-peak potential of cyclic voltammograms.

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. L. Koleva Gudeva, R. Gulaboski, E. Janevik-Ivanovska, F. Trajkova, V. Maksimova, *Electronic Journal of Biology*, 9 (**2013**) 29-36.