Voltammetry of Irreversible Surface Inactivation in Processes of Electrochemical Metal Alloys Dissolution

Pavle Apostoloski, Rubin Gulaboski,

[1]*Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia*

Abstract

This work considers a theoretical analysis of voltammetric behavior in electrochemical systems where metal alloy dissolution is accompanied by irreversible surface inactivation of a given metal present in analyzed metallic alloy. The study mainly focuses on the influence of kinetic and chemical rate parameters that govern the interplay between active dissolution and the progressive loss of reactive surface sites. Mathematical modeling within the framework of square-wave voltammetry was developed to describe the transient current responses under conditions of surface passivation and alloy component selectivity. The analysis demonstrates how the rate of surface inactivation, relative to electron-transfer kinetics affects peak currents, potential shifts, and hysteresis in voltammetric profiles. The proposed theoretical approach provides a mechanistic interpretation of experimentally observed phenomena in alloy corrosion and electrochemical dissolution, offering insights into processes where the active surface area decreases irreversibly during anodic or cathodic polarization. The model serves as a foundation for understanding surface deactivation effects in complex metal systems and contributes to more accurate diagnostics of corrosion and dissolution mechanisms in many alloys.

$$M(solid) + Y = MY_{\mathbf{(solid)}}$$

$$M(solid) - 2\,e^- = M^{2+}(aq)$$

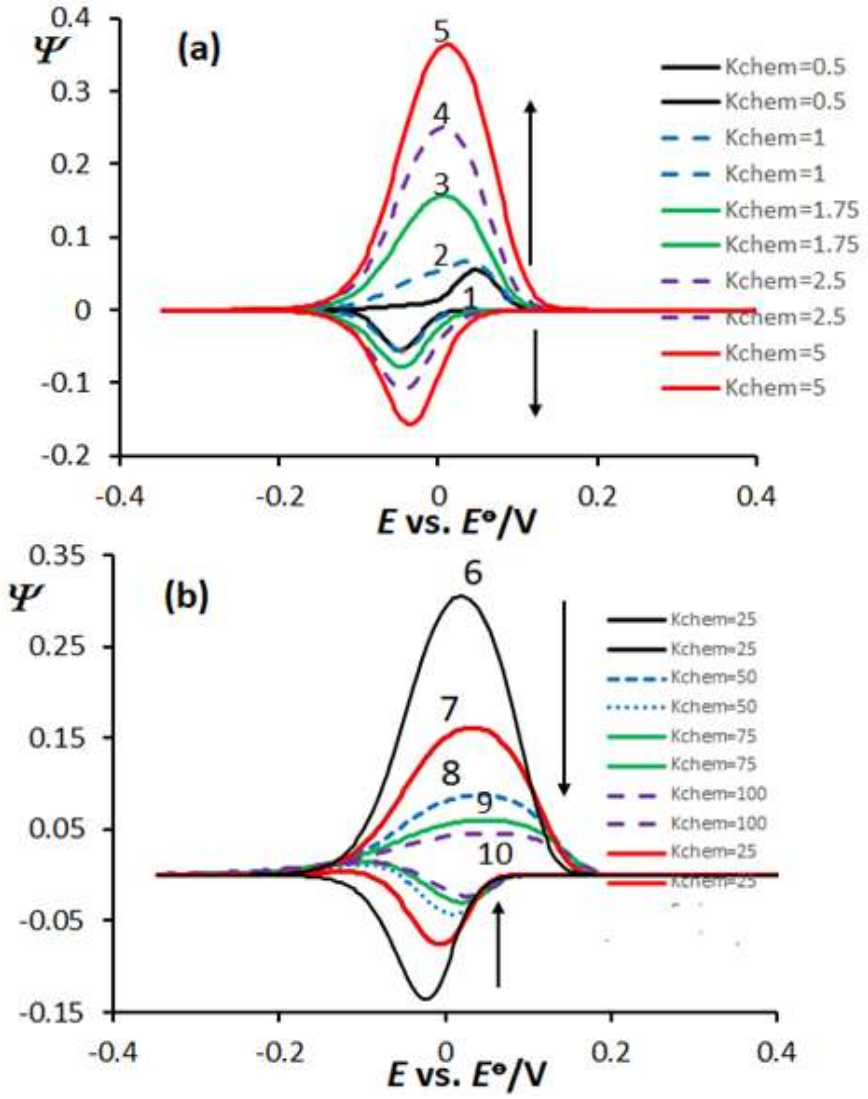


Figure 1. M(solid) - ne$^-$ ⇄ M^{n+}(aq) coupled by M(solid) + Y → MY(solid). Voltammograms are calculated ad dE = 2 mV α = 0.5 frequency of 50 Hz. Voltammograms feature the effect of the dimensionless chemical kinetic parameter (Kchem).

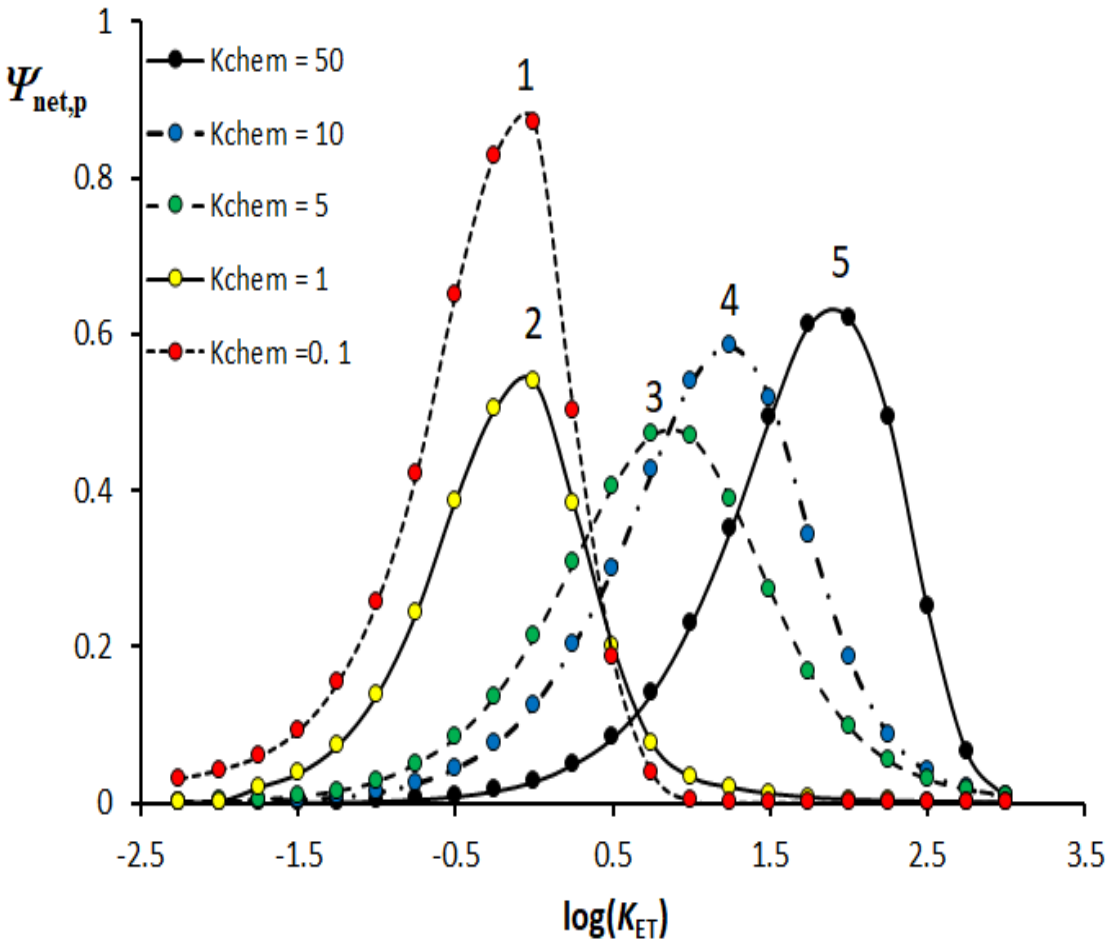
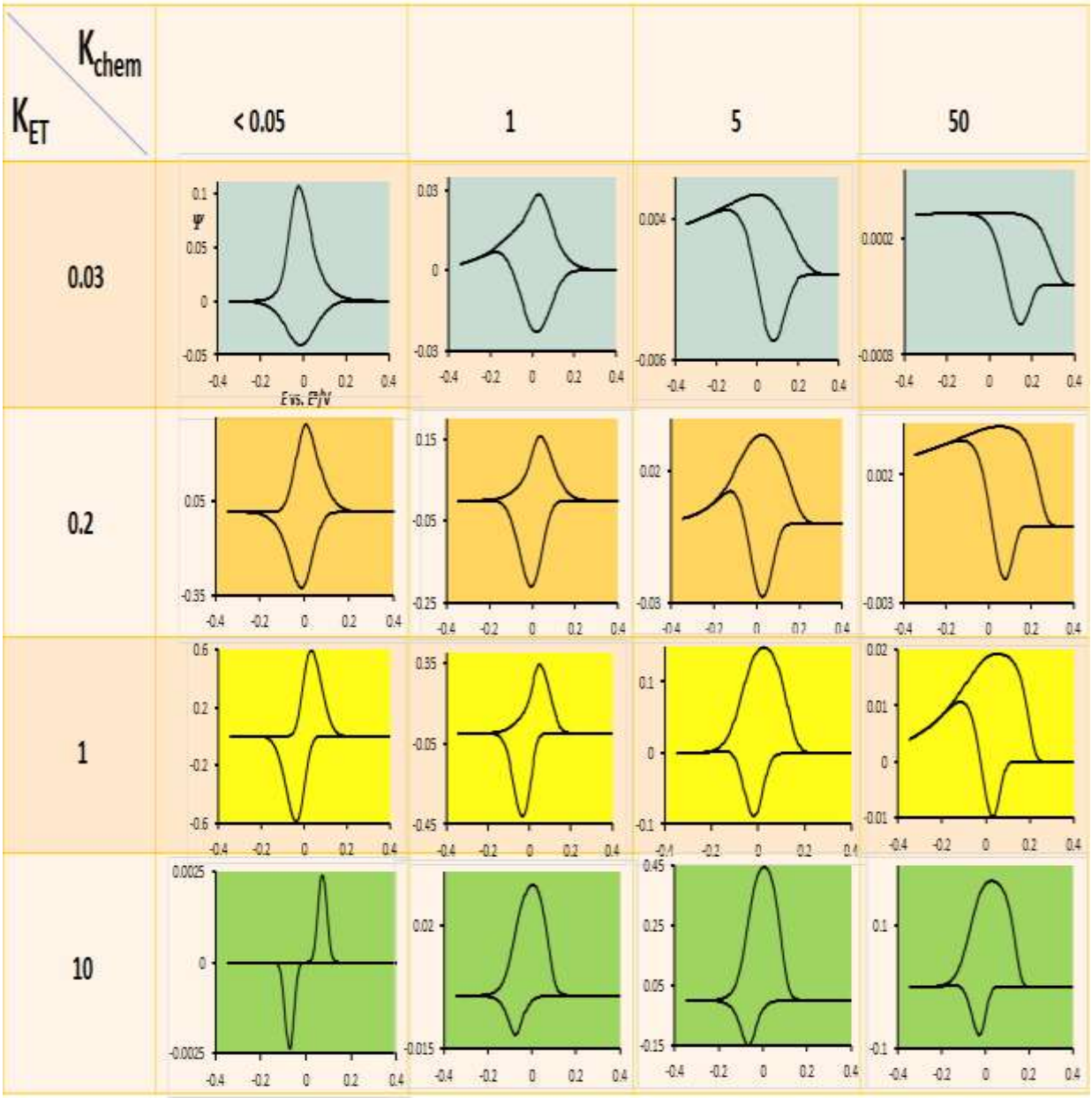


Figure 2. Voltammetric curves displaying the net-peak currents profiles in electrochemical decay of metal alloy (M(solid) - $ne^- \rightleftarrows M^{n+}(aq)$ showcasing the effect of concentration of the ligand "Y" (that affects the rate of irreversible chemical inactivation of given metal M) expressed via the magnitude of the chemical parameter $\boldsymbol{K_{chem}}$. Working curves are calculated at different kinetic regimes of the electron transfer step.

Table. Forward and backward current components of the square-wave voltammetric patterns calculated at different rates of electron transfer step and at different kinetics of irreversible chemical reaction. For the voltammograms displayed in this table, a square-wave amplitude of 80 mV and potential step of 4 mV were used. The electron transfer coefficient in all simulations was $\alpha = 0.5$.



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.