Theory in practice: Testing the limits of the Randles- Ševčík equation

Gabriel N. Meloni, Luiz F. Z. Felipe, Rafael S. Santos
Institute of Chemistry, University of São Paulo
gabriel.meloni@usp.br

The Randles-Ševčík equation[1,2] is notably one of the most known equations in electrochemistry, often used to diagnose or characterize the reversibility of an electrochemical system. Despite the continuous usage, one or more of its boundary conditions are often ignored. The most elusive of the boundary conditions is that it is an analytical solution for a 1-dimension diffusion problem (Figure 1A). At small electrode radii, radial diffusion at the edges significantly contributes to mass transport. The minimum size of a disk electrode to meet the 1D diffusion criteria was theorize by Compton *et al*,[3] but until now limits were not experimentally investigated. Here we employ 3D printing to fabricate disk electrodes with a range of radii and investigate the reversibility of the $[Ru(NH_3)_6]^{2+/3+}$ redox probe. We visualize and quantify, with the aid of numerical simulations, the contribution of radial diffusion to the overall mass transport and experimentally determine a spatial-temporal limit to the use of the Randles-Ševčík equation, showing that most electrode sizes used do not meet all boundary conditions (Figure 1B). We hope to demonstrate that accurate characterization of electrochemical processes requires a complete understanding of the equation's limitations, and that the use of the Randles-Ševčík equation is seemingly simple, requiring proper experimental care.

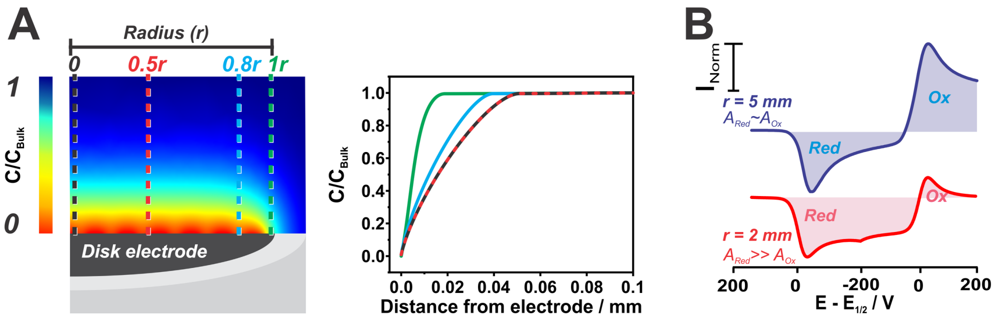

Figure 1: *Numerical simulation of the diffusion layer of a disk electrode with concentration profiles (right panel) calculated at four different locations over the electrode surface, market as dashed lines. (B) Integration of the area under the voltammetric curve of a 5 mm (top) and 2 mm (bottom) radius disk electrodes.*

Acknowledgments:

FAPESP processes: 2025/00970-7, 2024/14586-1 and 2021/00800-3

References:

[1] J. E. B. Randles, Trans. Faraday Soc. 1948, 44, 327–338. [2] A. Ševčík, Collect. Czechoslov. Chem. Commun. 1948, 13, 349–377. [3] K. Ngamchuea, S. Eloul, K. Tschulik, R. G. Compton, J. Solid State Electrochem. 2014, 18, 3251–3257.