Reactions in Droplets on Electrode Surfaces

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Compartmentalised chemistry takes place in a plethora of natural and artificial environments [1]. Examples of the former range from biology to geology and include gametes, synaptic vesicles, nucleoli, fluid inclusions, Pele's tears, *etc.* Artificial environments likewise have broad industrial applications, such as micelles in chemical emulsions, coacervates, in molten metal manufacturing, *etc*. This is a diverse utility of fluid droplets, and a key question revolves around how the chemical environment of the droplet impacts on its functional application.

For electrochemical systems, sessile droplets bathed by a fluid environment give rise to the opportunity for reactions at the three-phase boundary – the locus of the droplet edge in contact with both the electrode and the surrounding fluid, since this is where the current density is the greatest [2]. However, transport both inside and outside the droplet, effects due to reaction partitioning, surface tension gradients and interfacial kinetics can change the dynamics of droplet operations.

This presentation will first illustrate the interplay of factors affecting the dynamics of the electrochemical response of droplet-modified electrodes, highlighting the roles played by particular droplet chemistry, as well as the droplet volume, contact angle and distribution. These issues enable a critical assessment of claims of reaction rate acceleration of redox catalytic reactions within supported single droplets on electrode, as well as "thermodynamic dispersion" in protein-film voltammetry [3].

Acknowledgments

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References

[1] See, for example, G. Lloyd, R. S. Forgan (eds.), *Reactivity in Confined Spaces*, Royal Society of Chemistry, London, 2021.
[2] See, for example, F. Scholz, U. Schröder, R. Gulaboski, A. Doménech-Carbó, *Electrochemistry of Immobilised Particles and Droplets: Experiments with Three-Phase Electrodes*, 2nd edn., Springer, Heidelberg, 2015.
[3] See, for example, H. O. Lloyd-Laney, M. J. Robinson, A. M. Bond, A. Parkin, D. J. Gavaghan, A spotter's guide to dispersion in non-catalytic surface-confined voltammetry experiments, *J. Electroanal. Chem.*, 2021, **894**, 115204.