Electrolyte and Ionomer-Electrocatalyst Interactions – Electrochemical Diagnosis Tools and Applications

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Optimal electrocatalyst development cannot be achieved by focusing solely on the electrocatalyst itself. Indeed, reactions kinetics and thermodynamics depend not only on its intrinsic properties but also on the characteristics of the electrocatalyst/electrolyte interface. Recent years have seen a new surge in observations on how the electrolyte nature substantially influences a given reaction [1,2], to the extent that the electrolyte fine-tuning became equally important to the electrode properties. Furthermore, the development of industrially-compatible interfaces led to the near-universal integration of an ionomer within the catalytic layer, either as a binder or, in low-temperature fuel cells, as an ionic conductor. By embracing its 'electrolyte' nature, the ionomer started to alter the electrode reactivity [3,4] bringing the ionomer – electrocatalyst interactions at the forefront of new electrode/electrolyte interface development. This presentation gravitates around the development of electrochemical approaches and tools and their application to various cases of interest in the field of H_2 utilization. Specifically, it: (i) discusses the methodology and tools for studying electrolyte (namely, H_2SO_4 and H_3PO_4) – electrocatalyst interactions using conventional electrochemical approaches in rotating disk electrode and gas diffusion cell configurations, this in the presence of Nafion® or PWN (poly(2,3,5,6-tetrafluorostyrene-4-phosphonic acid). This conventional electrochemistry is then complemented with electrochemical impedance spectroscopy – and specifically, complex capacitance studies – to assess how the ionomer and electrolyte nature alter the frequency response of nanostructured electrodes; (ii) extends the aforementioned methodology toward a library of ionomers of interest for anion exchange membrane alkaline fuel cells, to evaluate their interactions with nanostructured platinum electrocatalysts and thus their applicability in industrial-like devices.

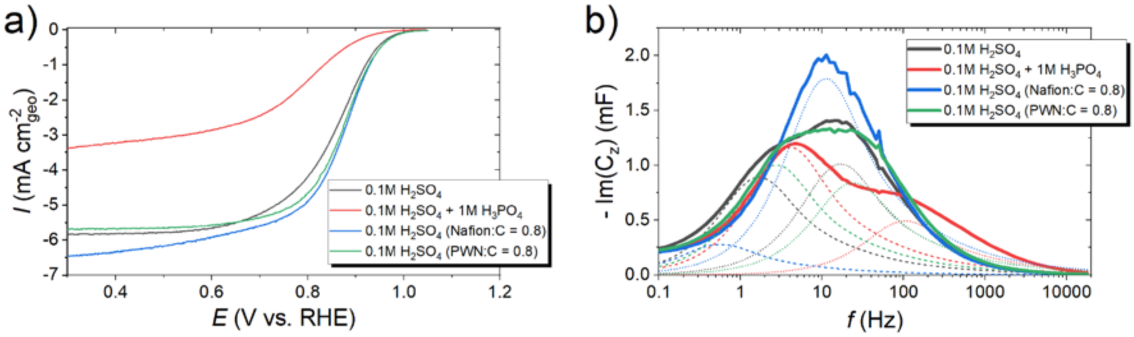

Figure 1: (a) Polarization curves for the oxygen reduction reaction of Pt/C as a as a function of electrolyte composition and ionomer to carbon ratio (I:C – when not indicated, I:C = 0) in the catalytic layer – T = 25°C, rotation rate = 1600 rpm, scan rate = 5 mV/s) and (b) associated complex capacitance patterns extracted from the electrochemical impedance spectroscopy analysis (at 0.26V *vs.* RHE, with the dotted lines corresponding to contribution of platinum nanoparticles localized within different regions, *e.g.*, macropores, mesopores, of the electrode porous network).

References: (1) Monteiro, M. C. O. *et al.* ACS Catal. 2021, 11, 14328–14335; (2) Marcandalli, G. *et al.* Acc. Chem. Res. 2022, 55, 1900–1911. (3) Matanovic, I. *et al.* J. Phys. Chem. Lett. 2017, 8, 4918–4924. (4) Fraser, K. *et al.* ChemCatChem 2024, 16, e202301304.

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Clean Hydrogen Partnership

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