

Influence of Acidity, Water and Temperature on the Double Layer Properties of Protic Ionic Liquids for Future Fuel Cell Applications

C. Korte, Y. Suo, K. Wippermann and Chr. Rodenbücher

Forschungszentrum Jülich, Institute of Energy Technology (IET-4: Electrochemical Process Engineering)

E-mail address: c.korte@fz-juelich.de

Polymer electrolyte membrane fuel cells (PEMFC) are a viable alternative to combustion engines and rechargeable batteries for automotive applications. However, the operating temperature at ambient pressure, using sulfonated fluoropolymers like NAFION®, is limited below 80 °C, as the proton conduction relies on the presence of water. Operation above 100 °C would allow a much more simplified system setup for water and heat management. This requires a non-aqueous protic electrolyte. Proton conducting ionic liquids (PIL) are promising candidates. [1,2]. However, the fuel cell relevant electrode reactions, oxygen reduction/hydrogen oxidation (ORR/HOR), are not as well understood as in aqueous electrolytes. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), chronoamperometry (CA) and steady state current measurements are employed to elucidate the double layer properties of the Pt electrode/PIL interface, kinetics and mechanism of the ORR. Three PILs with Brønsted-acidic cations $[\text{HA}^+][\text{X}^-]$, but different acidity are compared.

The first reduction step, including the proton transfer to the catalytic active sites on the electrode, is rate limiting. The presence of residual water $c(\text{H}_2\text{O})$, unavoidable at operation also >100 °C, is another important parameter, modifying the ordered structure of the electrochemical double layer. H_3O^+ is formed by protolysis with the high acidic PIL cations. In high acidic PIL, the HA^+ cations serve as a proton donor in particularly at low $c(\text{H}_2\text{O})$, whereas the role of H_3O^+ becomes more prominent at higher $c(\text{H}_2\text{O})$ [3]. In low acidic PILs, H_3O^+ is always the predominant proton donor. The onset potential/overpotential of the ORR in a PIL based fuel cell will depend on both, $c(\text{H}_2\text{O})$ and the PIL cation acidity.

According to EIS, at least two differential double layer capacitances are present, depending on cell potential U (vs. RHE), $c(\text{H}_2\text{O})$ and T . The double layer properties of high acidic PILs are significantly different compared to low acidic PILs. The differential capacitance is discussed, considering a mean field model, the presence of water and short range ion correlations, to provide deeper insights into the double layer structure of the Pt electrode/PIL interface. [4, 5]

References

1. K. Wippermann, J. Giffin, S. Kuhri, W. Lehnert and C. Korte, *Phys. Chem. Chem. Phys.* **19**, 24706 (2017).
2. K. Wippermann, Y. Suo and C. Korte, *J. Phys. Chem. C* **125**(8), 8 (2021)
3. H. Hou, H. M. Schütz, J. Giffin, K. Wippermann, X. Gao, A. Mariani, S. Passerini and C. Korte, *ACS Appl. Mater. Interfaces* **13**, 8370 (2021)
4. Z. A. H. Goodwin, G. Feng and A. A. Kornyshev, *Electrochim. Acta* **225**, 190 (2017)
5. J. Friedl, I. I. E. Markovits, M. Herpich, G. Feng, A. A. Kornyshev and U. Stimming, *ChemElectroChem* **4**, 216 (2017)