

# Electrode kinetics of ionic liquids as proton-conducting electrolytes for PEFC operating above 100 °C

Yingzhen Chen,<sup>a</sup> Christian Rodenbücher,<sup>a</sup> Klaus Wippermann,<sup>a</sup> Carsten Korte<sup>a</sup>

<sup>a</sup> Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, 52425 Jülich.  
y.chen@fz-juelich.de

Fuel cells have gained particular interest due to the demands for clean and sustainable energy sources. They can generate electricity with high efficiency using “green hydrogen”. Polymer electrolyte membrane fuel cells (PEMFC) have turned out to be the most viable alternative to combustion engines for automotive applications. However, PEMFCs using sulfonated fluoropolymers, e.g. NAFION®, whose proton conduction relies on the presence of water, limits the operating temperature below 80 °C (ambient pressure). A PEMFC operating at 100–120 °C would be more attractive, owing to a much more simplified system setup for water and heat management. This requires novel non-aqueous electrolytes. Protic ionic liquids (PIL) immobilised in a host polymer are considered as alternative membranes for future intermediate-temperature (“IT-”) PEMFCs. [1] Ionic liquids consist of bulky organic cations and anions of superacids, resulting in a low lattice energy and a low melting point. The structure of the electrical double layer is different to aqueous solutions, consisting of alternating cation and anion layers. [2] The knowledge of the cathodic oxygen reduction reaction (ORR) kinetics is essential for the further optimization of the PIL (ion) structure and properties for the use in future fuel cells.

In this study, we employed electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), chronoamperometry (CA) and steady state current measurements to elucidate the kinetics and possible mechanism of the ORR in PIL electrolytes with an Brønsted-acidic cation [HA<sup>+</sup>][X<sup>-</sup>]. Investigations on PILs with different cation acidity strongly suggest that the first reduction step including the proton transfer to the (catalytic) active sites on the electrode is mainly determining the ORR rate in these systems. The presence of residual water, unavoidable also at fuel cell operation >100 °C, is another important parameter. H<sub>2</sub>O modifies the ordered structure of the electrochemical double layer. Its protolysis equilibrium with an acidic PIL results in the formation of H<sub>3</sub>O<sup>+</sup> that serves as a proton donor in the rate determining step and thus influences the ORR kinetics. Highly acidic PIL cations serve as a proton donor as well, particularly at low H<sub>2</sub>O concentrations, whereas the role of H<sub>3</sub>O<sup>+</sup> as a proton donor in the ORR becomes more prominent at higher water concentrations [3]. In low acidic PILs, H<sub>3</sub>O<sup>+</sup> is the predominant proton donor and the ORR rate is significantly smaller resulting in considerably higher overpotentials. Thus, the onset potential of the ORR in a future IT-PEMFC will depend on both the concentration of residual water and the PIL cation acidity.

## References:

- [1] H. Hou, H.M. Schütz, J. Giffin, K. Wippermann, X. Gao, A. Mariani, S. Passerini and C. Korte, *ACS Appl. Mater. Interfaces* **13**(7) (2021) 8370–8382
- [2] C. Rodenbücher, Y. Chen, K. Wippermann, P.M. Kowalski, M. Giesen, D. Mayer, F. Hausen and C. Korte, *Int. J. Mol. Sci.* **22** (2021) 12653.
- [3] K. Wippermann, Y. Suo and C. Korte, *J. Phys. Chem. C* **125**(8) (2021) 4423–4435