Influence of temperature and water on phosphonium-based protic ionic liquids for Intermediate temperature PEMFCs

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Polymer electrolyte membrane fuel cells (PEMFCs) are a viable alternative to combustion engines and rechargeable batteries for automotive applications. The operating temperature of PEMFCs utilising sulfonated fluoropolymers as NAFION® is restricted to below 80 °C, as the presence of water is a prerequisite for proton conduction. At temperatures above 100 °C, the use of a non-aqueous protic electrolyte would facilitate significantly the water and heat management. Protic ionic liquids (PILs) can serve as effective substitutes. PILs are molten salts characterised by high thermal stability and high conductivity. Ammonium-based cation PILs have demonstrated a rapid oxygen reduction reaction (ORR) kinetics, namely the main bottleneck of the electrodic redox processes, compared with other electrolytes, such as phosphoric acid. [1-2] These results are attributed to the pronounced proton-donating capability of the acid PIL cations and the enhanced oxygen permeability arising from the more apolar character of the electrolyte bulk. [3]

In this study, phosphonium-based PILs (PPILs) are investigated as electrolytes for the application in future intermediate temperature PEMFCs for a temperature range of 80–160 °C). The PPILs have already shown in previous studies higher thermal stability and oxygen permeability compared to ammonium-based PILs, due to heavier cations and even higher apolar character due to the presence of the aliphatic phosphonic functional group. In this study, three PPILs, comprising superacid anion triflate [TfO] and quaternary acidic phosphonium cations trioctyl(3-sulfopropyl)phosphonium [tOP], tributyl(4-sulfobutyl)phosphonium [tBB] and tributyl-(3-sulfopropyl)phosphonium [tBP], are investigated by linear sweep voltametry (LSV) regarding their ORR performances. The investigations were conducted in the temperature range between 80–120 °C and at different water content at an water partial pressure between 0–15 kPa to simulate the expected operating conditions. The PPILs show higher ORR current densities at increasing temperature and water content than the ammonium-based PIL [2-Sema][TfO], a well-studied electrolyte with promising electrochemical performance. These features of the PPILs are originate from the high acidity of the cation acting as proton donor in the ORR combined with a high oxygen permeability, ensuring a readily accessible oxygen supply for the cathodic reaction and thereby promoting faster reaction kinetics. Additional electrochemical impedance analyses (EIS) have also shown a higher current density due to the (rate limiting) charge transfer process, inline with result from LSV. Moreover, also the areal capacity of the double layer related process is higher. These results indicate that PPILs are potential candidates for fuel cell applications at elevated temperatures.

References

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