Effects of protic ionic liquids on the oxygen reduction reaction - a key issue in the development of intermediate-temperature polymer-electrolyte fuel cells

Klaus Wippermann and Carsten Korte

Abstract

Intermediate-temperature polymer-electrolyte fuel cells (IT-PEFCs), operated at an elevated temperature of ≈120 °C, would enable simplified system design and a potential increase in fuel cell performance compared to state-of-the-art low-temperature (LT-)PEFCs. As LT-PEFC membranes rely on the presence of water and high-temperature (HT-)PEFCs suffer from sluggish oxygen reduction reaction (ORR) kinetics, alternative materials must be developed. Promising candidates are protic ionic liquids (PILs) immobilized in, *e.g.*, a host polymer. PILs' properties, such as weak ion adsorption, high acidity of the proton-carrying ion, an excess of the anion precursor, and a high oxygen diffusivity and solubility, are favorable for achieving high ORR rates. Concepts proposed in the literature for incorporating PILs into MEA components are presented herein, and their utility for future IT-PEFCs is discussed.

Addresses

Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research – Electrochemical
Process Engineering (IEK-14), 52425 Jülich, Germany

Corresponding author

Wippermann, Klaus (k.wippermann@fz-juelich.de)

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Introduction

State-of-the-art polymer-electrolyte fuel cells (PEFCs) are based on sulfonated fluoropolymer membranes. The proton conductivity of these materials (*e.g.*, NAFION®) critically depends on the presence of liquid water. Therefore, the ambient pressure limits the operating temperature to a maximum of 80 °C. This type of fuel cell can also be called an “LT-PEFC” (low-temperature PEFC). LT-PEFCs have achieved a reasonable level of performance and durability thus far. However, cost reduction remains an issue. An effective way to reduce system costs would be to increase the operating temperature beyond 100 °C. This would enable a simplified design of a PEFC system without the need for active water management, effective cooling, the utilization of waste heat, and a lower sensitivity against feed gas impurities. High-temperature PEFCs (HT-PEFCs) based on phosphoric acid-doped polybenzimidazole (PBI) membranes are operated in a temperature range of 160–180 °C. Unfortunately, their poor performance, primarily due to sluggish ORR kinetics caused by a poisoning of the platinum catalysts by phosphate ions, prevents their commercialization on a larger-scale. An intermediate-temperature PEFC (IT-PEFC), operable at about 120 °C, would be interesting, especially for automotive applications. The challenge is the development of new, alternative non-aqueous proton-conducting electrolytes and membranes that meet the performance and durability requirements, even under almost water-free conditions.

In 2005, Kudo et al. were the first to use the term “intermediate-temperature fuel cell” in the context of PEFCs [1,2]. For a proton-conducting electrolyte, Kudo et al. employed protic ionic liquids (PILs). Ionic liquids are mostly suitable as electrolytes because of their small vapor pressure and high chemical and thermal stability. A PIL is an ionic liquid with a proton-carrying Brønstedt acidic ion. PILs with a Brønstedt acidic cation can be prepared by protonating an (organic) base (B) by a strong acid (HA), *i.e.*, $B + HA \rightarrow BH^+ + A^-$.[1] Two years earlier, Watanabe et al. demonstrated the performance principles of PILs for the oxygen reduction reaction (ORR) that takes place at fuel cell cathodes [3,4]. Since then, the electrochemical and bulk properties of numerous PILs have been investigated [5-39].

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[1] There are also PILs with a neutral organic cation (quaternary ammonium or phosphonium) and an acidic anion, *e.g.*, $NR_4^+ \cdot HSO_4^-$.

Moreover, reviews of ionic liquids in electrocatalysis [40] and ORR [41], as well as PIL-based membranes for PEM fuel cells [42], have also been published. An important topic in these studies [1-39] is the effect of the PILs' properties on the oxygen reduction reaction, which is also the focus of this review. Detailed analyses of ORR kinetics are crucial, as the ORR remains the bottleneck in the reaction kinetics of PEFCs and an improvement in the ORR rate would substantially enhance overall fuel cell performance. The scope of the above-mentioned literature covers the investigation of model systems with (ideal) model electrodes, porous electrodes, as well as complete single cells. Accordingly, we start with a review of ORR kinetics and mechanisms exerted on platinum in liquid PILs, and then briefly discuss studies of ORR kinetics with PILs as fuel cell components.

ORR with PILs as liquid electrolytes

Current ORR studies on Pt in PIL electrolytes have usually revealed a four-electron mechanism ($O_2 + 4\ H^+ + 4e^- \rightarrow H_2O$) [3,4,18,23-25,32,36,39], possibly *via* an associative adsorption of molecular oxygen [39]. However, this mechanism cannot be generalized, and does not exclude the formation of hydrogen peroxide or a dissociative reaction path *via* atomic oxygen. For example, in the case of Ethylammonium nitrate (EAN),[2] Khan et al. found a two-electron mechanism with only hydrogen peroxide as a product. The overall ORR reaction proceeds via several single steps involving various adsorbed oxygen species. The first reduction step, which includes the protonation of the oxygen molecule [39], and the last one, entailing the reductive desorption of the adsorbed hydroxide [37], have been identified as rate-determining.

The ORR studies on PIL electrolytes may be categorized according to the following categories: (*i*) structure of the cations [1,2,14-16,19,20,25,36,38,39] and anions [1,2,10,14-16,19,20,25,38]; (*ii*) the acidity (pK_a) of the cation [39]; (*iii*) the difference in acidity of the strong acid HA and the cation BH^+, *i.e.*, ΔpK_a [15,16,19]; (*iv*) a non-stoichiometry of the PIL, which means either an excess of the anion

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[2] Chemical names and structures of the acronyms of PIL cations and anions and polymer membranes mentioned in the manuscript can be found in the Supporting Information (see Figures S1 and S2).

precursor HA [1,2,25] or the cation precursor B [6]; and (*v*) the influence of additives like water [6,24,36,38,39] or phosphoric acid [9]. Because of the interdependencies of these properties, the unambiguous allocation of a single property to a distinctive effect on the ORR kinetics is a challenging task. A schematic representation of examples of effects (*i*)–(*v*) is given in Fig. 1.

(i) Although several works about PILs with different ion structures have been published (see above), extended and systematic studies, that allow one to draw general conclusions on the effect of structural parameters of complex PIL ions on the ORR kinetics, are still lacking. Munakata et al. found an improved ORR performance through increasing the fluoroalkyl chain length in PILs with a bis-(fluoroalkylsulfon)-imide anion [10]. Even though they attributed this effect to a decreasing specific adsorption of the anion on the Pt (less of a blocking effect), they acknowledged that other factors, such as solubility and the diffusivity of oxygen may also play a role. This example illustrates the difficulty of identifying clear relationships within these complex systems.

(ii) Thermodynamically, a high cation acidity enhances the proton donor ability in the ORR and the generation of H_3O^+—a highly effective proton donor. In our recent publication [39], we demonstrated that a high cation acidity is advantageous from a kinetic point of view: the ORR rate clearly increases in the order of increasing cation acidity, *i.e.*, [$DEMA^+$] ($pK_a = 10.55$) < [$1\text{-}EIm^+$] ($pK_a = 7.3$) < [$2\text{-}SEMA^+$] ($pK_a = 0.94$).

(iii) Miran et al. [15,16] correlated the open circuit potential (OCP), a measure for the ORR activity, with ΔpK_a, the difference in the pK_a values of HA and BH^+. They found an OCP maximum of $\Delta pK_a \approx$ 17–18. Their explanation appears plausible: if ΔpK_a is too low, the proton transfer from HA to B is not quantitative and the residual, neutral cation precursor B may then poison the catalyst surface [15]. Conversely, if ΔpK_a is too high, particularly the pK_a value of the cation, the cation is a poor proton donor in the ORR. Both will slow down the ORR kinetics, decrease the exchange current density, and increase the overpotential. As a consequence, acidic PIL cations, BH^+, must be combined with highly acidic (super)acids, HA, to obtain intermediate ΔpK_a values and high ORR activities.

(iv) A non-stoichiometry of the molar 1:1 ratio of the anion and cation precursors in the PILs, whether accidentally or through an intended addition of HA or B, can dramatically change the ORR activity. Goodwin et al. have demonstrated that the addition of only 100 mM triflic acid (TfOH) to [DEMA][TfO] results in an 800 mV shift in the ORR onset potential [25]. This is explained by a change from a poor proton donor ($[DEMA^+]$) to a good one (TfOH) in the ORR. Non-stoichiometries could also explain the very different ORR activities among Pt electrodes that have been reported for [DEMA][TfO] [9,13,15,16,18,19,25,36,39], apart from differences in temperature and water content.

(v) As water is produced at the fuel cell cathode, a steady-state amount of 20–30 mol% (~1–2 wt%) of water can be estimated for the operation of future IT-PEFCs. In a protolysis equilibrium with the PIL cation, the fairly good proton donor H_3O^+ is generated. Moreover, the increase in proton conductivity and oxygen diffusivity accelerates the proton and oxygen transport to the active sites [43]. On the other hand, water molecules and non-reactive oxide species originating from the oxidative reaction of Pt and water may block active sites. Hence, the generation of water has a large influence on the ORR kinetics, the bulk properties of the PIL, and therefore the fuel cell performance. Thus, it is noteworthy that hardly any studies have addressed this topic. In our recent publication, we reported a minimum of the ORR rate constant of about 30 mol% water for acidic [2-SEMA][TfO] that can be explained through the complex overlap of the effects mentioned above.

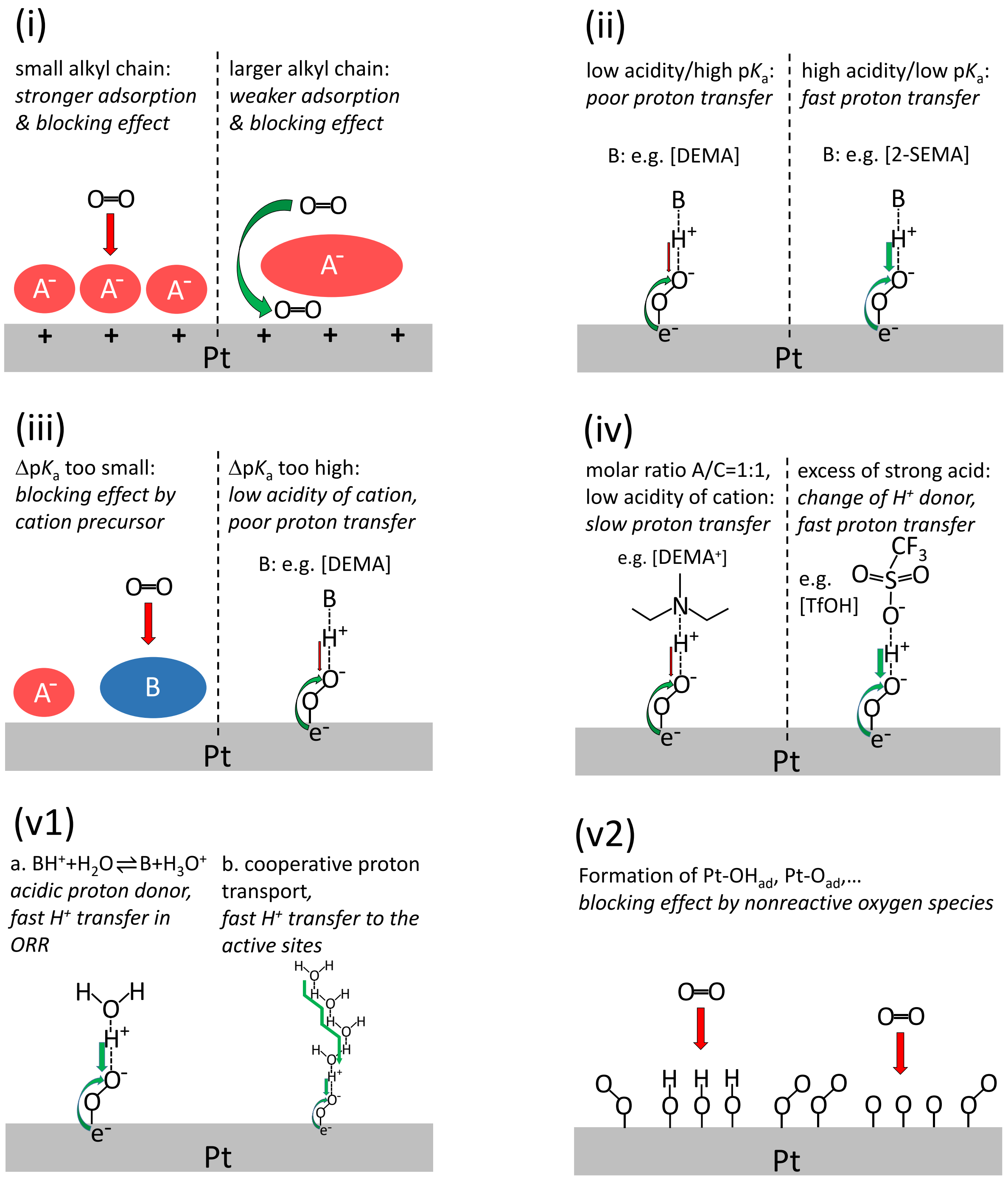

Figure 1. Schematic of the effects caused by different properties of PILs: (*i*) structure of the anion; (*ii*) acidity of the cation; (*iii*) ΔpK_a of the cation and anion precursor; (*iv*) non-stoichiometry (excess of the anion precursor), (*v*1)/(*v*2) advantages and disadvantages of residual water

ORR with PILs as fuel cell components

Another step in the R&D of future IT-PEFCs is the development of polymer membranes, gas diffusion electrodes and, finally, MEAs (single cells) based on protic ionic liquids. Whereas a number of studies have been published on polymer membranes based on PILs and PIL-containing MEAs (see e.g. the reviews of Elwan et al.[42] and Ebrahimi et al. [44]), there have been only a few ORR studies on PIL-containing MEAs at temperatures higher than 100 °C and under dry conditions [8,12,37]. The studies on PILs as fuel cell components including the investigation of the ORR comprise PILs that are part of (*i*) composite membranes [8,12]; (*ii*) of dispersed polymers as catalyst binders [35,37]; or (*iii*) of the catalysts [11,17,22,26-31,33,34].

Currently, single cells based on PILs without humidification of the H_2/O_2 feed gases and operating temperatures above 100 °C yielded maximum power densities of up to 420 mW/cm² (Li et al. [45]). This performance was achieved at 180°C by using a composite NAFION®/nano-silica/hydroxyl ionic liquid membrane sandwiched between commercial gas diffusion electrodes with carbon-supported Pt catalyst. The latter also applies to the MEA prepared by Lee et al. [8], who reported a maximum power density of 63 mW/cm²@120 °C with a composite SPI-[DEMA][TfO] membrane (see below). By contrast, Guo et al. [37] achieved ≈70 mW/cm²@160 °C by using a common, phosphoric acid doped PBI membrane sandwiched between commercial Pt/C electrodes prepared with a PIL grafted PBI binder (see below). However, even the highest value achieved so far is considerably smaller than the values of more than 1 W/cm² reported for common LT-PEFCs. First durability tests seem promising, since they reveal a fairly stable performance (Lee e al. [8]: open circuit voltage ≈ 0.75 V over a period of 230 h, Li et al. [45]: cell voltage of 0.72V @300 mA/cm²/160°C over a period of ≈100 h). The PIL-modified porous electrodes (see (*ii*) and (*iii*)) are based on carbon-supported Pt catalysts [22,26-28,31,35,37], Pt alloys such as NiPt [11,17], PtFeNi [30], and PtNiMo [29] or nitrogen-doped carbon (NC) catalysts such as FeNC [33] and ZnCoNC [34].

In the case of (*i*) and (*ii*), common perfluorosulfonic acid (PFSA) membranes or ionomers such as NAFION® are substituted by PIL-based materials. This includes composite membranes made of sulfonated polyimide (SPI) and [DEMA][TfO] [8,12], PIL-grafted polybenzimidazole (PBI) or NAFION®/nano-silica/hydroxyl ionic liquid [45], as well as proton-conducting binder materials among the catalyst layers [35,37]. The binder forms a 3-dimensional network of proton conducting paths that are in contact with catalyst particles throughout the catalyst layer. Since the supply or removal of protons to/from the catalyst is essential for the electrochemical reactions in PEM fuel cells, this means that not only the catalyst particles in direct contact to the membrane, but also those in inner parts of the catalyst layer can be utilized. This leads to an extension of the reaction zone and an increase in performance. Yan et al. substituted the NAFION® ionomer by a polymerized PIL, poly(DMVBAn-TfO-co-Stm), and found an increase in the active surface of the carbon-supported Pt catalyst and ORR performance [35]. They explained these findings by reference to the suppression of nonreactive oxygen species and accelerated oxygen transport due to the hydrophobic nature and structure of the polymerized PILs. Guo et al. [37] employed polybenzimidazole (PBI) grafted by PILs. In the case of PILs with $[\mathrm{TfO}]^-$ (‚PBI-F'), they found a significant increase in ORR performance compared to NAFION®. Despite the fact that the active surface decreases if NAFION® is replaced by PBI-F, the surface coverage of hydroxide also decreases. This is attributed to faster desorption of OH_{ad} and leads to an enhanced ORR rate.

Concept (*iii*) includes the impregnation of porous catalyst particles by PILs, *e.g.*, by simply using capillary forces [11,17] or by vacuum-assisted intrusion [22,26,29,34]. The typical thickness of the resulting PIL layers is ≈1–3 nm [17,26,31,33], although Zhang et al. [22] have estimated an average thickness of ≈1–15 nm, depending on the degree of pore filling. Independent of the catalyst used, the PIL films have a beneficial effect on both the ORR kinetics and catalyst durability. The kinetic effect is generally attributed to the reduction in coverage of non-reactive oxygen species that occupy active sites. For instance, the impregnation of a commercial carbon-supported Pt catalyst by [MTBD][NTf2] results in a positive shift of the half wave potential of ORR by ≈30 mV [22]. The durability effect of the PIL films is due to the suppression of both the agglomeration of catalyst particles and carbon corrosion. The latter effect has been explained in terms of the rejection of water by the hydrophobic PILs, which is crucial for Pt oxidation and the dissolution of oxides [26]. According to Huang et al., the loss in the electrochemically-active area following an accelerated aging test can be reduced from ≈17% (Pt/C without PIL) to ≈3% (Pt/C-[MTBD][C4F9SO3]). The inhibiting effect of ionic liquids is especially important because degradation processes such as Pt dissolution, agglomeration of Pt particles and carbon corrosion become faster at elevated temperatures.

Although the concept of catalyst impregnation has only been proven at low temperatures, it could also be promising for temperatures above 100 °C, provided that the PILs are thermally-stable and no degradation of the PIL film occurs. Defined, immobilized, and stable PIL domains are crucial in optimizing the porous structure of the catalyst layers for achieving high fuel cell performance. In contrast, an uncontrolled, inhomogeneous distribution of PILs may cause pore flooding and deteriorated oxygen (gas) transport to the active catalyst sites. Undesirable flooding effects caused by mobile phosphoric acid are well-known from HT-PEFCs [46].

Conclusions

In this study, we reviewed the effects of PILs on the ORR in the (Pt) catalyst / PIL interface. The PIL was either used as a liquid electrolyte or part of a fuel cell component. It turned out that PIL-based membranes and ionomers are promising components for future IT-PEFCs operating >100 °C. Although various concepts have been tested, fuel cell performance, in particular the ORR kinetics, must be substantially improved. Studies on the effects of PIL properties on overall electrochemical fuel cell performance have emphasized the importance of fast ORR kinetics, in addition to high protonic conductivity. A better understanding of the influence of proton donor ability and oxygen transport/solubility is necessary to improve PILs with regard to ORR performance, as well as the bulk properties. Future R&D work on IT-PEFCs should also aim at the development of highly conductive PIL-based membranes and a defined structure of PIL domains in catalysts and ionomers in order to avoid uncontrolled flooding of the pores by liquid PILs. These efforts seem worthwhile, as the elevated operating temperatures give future IT-PEFCs clear advantages over common low-temperature PEFCs.

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