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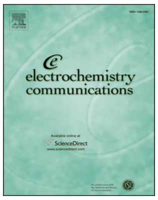

Short communication

Fluoroalkyl phosphoric acid derivatives — Model compounds to study the adsorption of electrolyte species on polycrystalline platinum

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ABSTRACT

The slow oxygen reduction reaction (ORR) in concentrated phosphoric acid remains a major technological challenge for future development of phosphoric acid fuel cells (PAFCs) as well as its congener the high-temperature proton exchange membrane fuel cells (HT-PEMFCs). It is generally accepted that adsorption of molecular or anionic species from the concentrated phosphoric acid electrolyte hinders ORR by blocking active sites on the catalyst surface. Aiming to better understand the adsorption mechanisms, we conducted a systematic study employing various types of perfluoroalkylated derivatives of phosphoric acid, in which one or two hydroxyl groups of phosphoric acid were substituted by perfluoroalkyl chains of different lengths. We evaluated these model electrolytes for their adsorption behavior and influence on ORR on a polycrystalline platinum surface by dosing small amounts of these acids to a 0.5 M perchloric acid solution. By means of cyclic voltammetry (CV), significant changes in the characteristic features of the pristine Pt voltammogram were observed. ORR kinetic currents measured by rotating disk electrode (RDE) were found to be strongly dependent on the molecular structure, particularly on the number of hydroxyl coordination sites and negative charge-density of the bis(perfluoroalkyl)-phosphinic or perfluoroalkyl-phosphonic acids added to the electrolyte.

1. Introduction

High-temperature proton exchange membrane fuel cells (HT-PEMFCs) are of growing interest in recent years because of the demand for power sources of clean energy. Compared with a conventional low-temperature PEMFC, high-temperature operation, in the range from 150 °C to 200 °C, leads to certain advantages like higher tolerance to fuel impurities and simplification of thermal and water management. However, HT-PEMFC cannot be operated with the Nafion electrolyte widely used for PEMFC due to its low proton conductivity under anhydrous conditions [1]. Concentrated phosphoric acid as a standard electrolyte exhibits excellent thermal and chemical stability combined with high proton conductivity under operating conditions typical for HT-PEMFC. Despite having desirable physical and chemical properties, sluggish ORR rate makes the use of phosphoric acid as fuel cell electrolyte problematic. This can be attributed to several reasons like low proton activity (acidity) of phosphoric acid and low oxygen solubility in this electrolyte as well as adsorption of phosphate species on the catalyst surface [2]. To overcome these drawbacks, novel compounds like trifluoromethane-sulfonic acid (TFMSA) [3–5] and a variety of salts derived from fluorinated compounds [6–9] were evaluated as alternative electrolytes or electrolyte additives, respectively. However, they turned out to be impractical because of undesirable physical properties at operation temperatures of a HT-PEMFC. A key task to improve fuel cell performance is therefore to identify alternative electrolytes that exhibit a low vapor pressure and are thermally and electrochemically stable. Recently Merck KGaA (Darmstadt, Germany) in cooperation with Willner group (University of Wuppertal) has developed a practical synthesis of perfluoroalkyl-phosphonic and bis(perfluoroalkyl)-phosphinic acids with different lengths of perfluoroalkyl chains (C2 and C4) [10] as presented in Fig. 1. They were found to exhibit both high proton conductivity under anhydrous condition [11,12] and high oxygen solubility [5]. These compounds are promising candidates as a new type of electrolytes for HT-PEMFC [11,12] and are also ideal model systems to study the effects of adsorbates on the ORR activity.

Here, we report experimental evidences obtained by means of cyclic voltammetry (CV) and rotating disk electrode (RDE), that demonstrate the stability of these perfluoroalkyl phosphorus acids over a wide potential range. Bis(perfluoroalkyl)-phosphinic acids appeared to be particularly promising because they were found to be almost non-adsorbing on a polycrystalline platinum surface. The influence of

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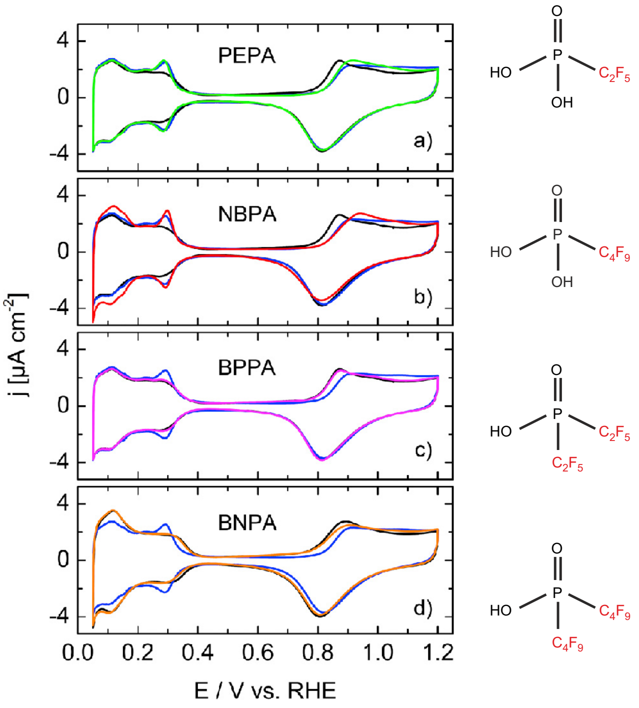

Fig. 1. Cyclic voltammograms of a polycrystalline Pt electrode in 0.5 M $HClO_4$ with an additive concentration of 1 mM for a) pentafluoroethyl-phosphonic acid (PEPA), b) nonafluorobutyl-phosphonic acid (NBPA), c) bis(pentafluoroethyl)-phosphinic acid (BPPA), and d) bis(nonafluorobutyl)-phosphinic acid (BNPA) compared to pristine perchloric acid (0.5 M) and 1 mM H_3PO_4. Potential scan rate 50 mV s^{-1}.

these compounds on the ORR is discussed and an adsorption model for the studied perfluoroalkylated acids is proposed.

2. Experimental

The RDE setup (Pine Instrument, USA) was equipped with a platinum disk electrode inserted in a cylindrical polytetrafluoroethylene holder. Measurements were performed in a glass cell using a three electrode setup. The reference and counter electrodes were a custom-made reversible hydrogen electrode (RHE) [13] and a Pt foil of adequate surface area, respectively. Oxygen saturated 0.5 M $HClO_4$ (Merck suprapur) solution was used as the base electrolyte for the RDE measurements. Prior to each experiment, the cell was thoroughly rinsed with ultrapure water (6 μS m^{-1}) to prevent contamination of the Pt disk.

Preconditioning of the working electrode was done by scanning the disk potential repeatedly between 0.05 V and 1.2 V at a scan rate of 100 mV s^{-1} to remove residual impurities while the electrolyte was continuously purged with high-purity argon. After the cleanliness of the system was carefully checked by CV, the electrolyte was purged with high-purity oxygen to saturation. Perfluoroalkylated phosphorus acids were added to the host solution to a final concentration of 1 mM. Polarization curves for the ORR (Fig. 2, solid lines) were obtained from the RDE data by subtracting the background current contribution recorded in the Ar-purged electrolyte, while mass transfer corrected current densities j_k (Fig. 2, dashed lines) were calculated from the Koutecký–Levich equation [14]. All reported values, unless specified differently, refer to a fixed potential of 0.9 V RHE at a rotation rate of 900 rpm for the Pt disk. Perfluoroalkyl phosphorus acids were provided by Merck KGaA (Darmstadt, Germany) and used without further purification.

3. Results and discussion

Fig. 1 reveals the effects of different perfluoroalkylated acids on the cyclic voltammograms. The influence of phosphate adsorption on the CV has been studied before in a different milieu [15,16]. Our results were obtained by adjusting a concentration of 1 mM of the studied perfluoroalkyl phosphorus acid in a host solution of 0.5 M perchloric acid, which is considered as a non-adsorbing electrolyte [17,18]. Significant changes in the hydrogen desorption and oxygen adsorption regions on the cyclic voltammogram were observed. These trends correlate with the molecular structure of the perfluoroalkylated phosphorus acids. In comparison to perchloric acid, the half wave potentials of the oxide formation peak are shifted to more positive potentials by 26 mV and 28 mV in the case of pentafluoroethyl-phosphonic acid (PEPA) and nonafluorobutyl-phosphonic acid (NBPA), respectively. This is commonly explained by the blocking of Pt adsorption sites by species from the electrolyte [19].

In the potential region of hydrogen adsorption/desorption, a sharp peak (0.29 V vs. RHE) was observed with a concentration of 1 mM of PEPA, NBPA and H_3PO_4 (Fig. 1). With increasing concentration, the hydrogen adsorption/desorption peak shifts to more negative potentials, probably due to an increase of surface concentration of the additive. The appearance of the peak at 0.29 V can most likely be attributed to stronger interactions of specifically adsorbed anionic species with hydrogen upd-sites compared to perchlorate anions. Furthermore, lower and flatter currents in the double layer region from 0.5 V to 0.75 V were observed in the case of PEPA or NBPA comparing to perchloric acid, possibly due to adsorption of anionic species competing with water adsorption. With a concentration of 1 mM of bis(pentafluoroethyl)-phosphinic acid (BPPA) or bis(nonafluorobutyl)-phosphinic acid (BNPA) in the host solution, the CV remained almost unaffected comparing to pristine perchloric acid (Fig. 1). This can be explained by relatively weak bis(perfluoroalkyl)-phosphinate-anion adsorption in this case. Fig. 2 shows changes in the ORR kinetic current densities for 1 mM of various perfluoroalkyl phosphorus acids in the host perchloric acid solution saturated with oxygen. The reported values are referred to a potential of 0.9 V RHE and serve as a measure for electro-catalytic activity. The result of pristine 0.5 M perchloric acid is also shown for comparison. The results clearly indicate that the catalytic activity can be correlated with the chemical structure of the perfluoroalkyl phosphorus acid additives. The ORR activity increases from H_3PO_4 to bis(perfluoroalkyl)-phosphinic acid with successive substitution of hydroxyl groups by perfluoroalkyl chains. By this substitution the number of proton-donating groups is reduced, while the acidity of the corresponding acid is increased [11]. Compared with H_3PO_4, the introduction of one perfluoroalkyl group to phosphorus (the case of perfluoroalkyl-phosphonic acids) results in approximately double ORR activity. In the case of perfluoroalkylated phosphinic acids the ORR activity is more than five times higher. This can be explained by reduced blocking of catalytically active sites on the Pt surface associated with weaker adsorption of perfluoroalkyl phosphorus acid species. On the other hand, no significant dependence of the electro-catalytic ORR activity on perfluoroalkyl chain length was observed within the evaluated substances. This indicates that the difference in the number of coordination sites of perfluoroalkyl phosphorus acids is the major reason for this phenomenon. These observations can be explained on a microscopic level by the proposed adsorption model shown in Fig. 3, which illustrates the most likely adsorption geometries for perfluoroalkylated phosphorus acids. Phosphate is assumed to be adsorbed on threefold sites of the Pt surface, representing an energetically stable configuration. Bis(perfluoroalkyl)-phosphinate and perfluoroalkyl-phosphonate are much less nucleophilic in comparison to phosphate anion that reduces their interaction with the Pt surface resulting in weaker adsorption.

Our results suggest that the adsorption probability of the evaluated additives mainly depends on the number of negatively charged sites (hydroxyl-groups) and the electron density on these active sites. The length of the fluoroalkyl chain only marginally affects the kinetic