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Evaluation of temperature and electrolyte concentration dependent Oxygen solubility and diffusivity in phosphoric acid

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ABSTRACT

Reactant diffusion and solubility is of utmost important for providing sufficient reactant concentrations at a catalytic active surface. In high temperature proton exchange membrane fuel cells (HT-PEMFCs) the electrolyte consists of concentrated phosphoric acid embedded into a polybenzimidazole (PBI) membrane. Despite the elevated operation temperature of 150 °C, the observed oxygen reduction reaction (ORR) rates in HT-PEMFCs are significantly lower than in low temperature PEMFCs. Reduced reactant transport in combination with site blocking is often mentioned as possible inhibition factors. As a step towards studying the ORR under realistic conditions in half-cell setups, in the present study we investigate the oxygen solubility and diffusivity in diluted phosphoric acid electrolyte in a temperature range of 5 to 80 °C. The presented work demonstrates and discusses under which conditions reliable data for these constants can be obtained. In particular it is shown that the product of oxygen solubility and diffusivity, which determines the oxygen mass transport, first increases as function of temperature, but then decreases again above 60 °C. It seems that the decrease in oxygen solubility at higher temperatures is correlated to an increase in the apparent ORR activation energy.

1. Introduction

Energy conversion and storage devices are key components for renewable energy supply. To align demand and supply, renewable energy can be stored in chemical bonds, e.g. by electrolysis of water to hydrogen and oxygen, and later reconverted to electricity using a fuel cell. For such a scheme to be meaningful high conversion efficiencies are mandatory; i.e. the activity of the applied electrocatalysts must be high. Phosphoric acid (PA) fuel cells were one of the first commercially applied fuel cells. The modern day phosphoric acid fuel cell – the high temperature proton exchange membrane fuel cell (HT-PEMFC) – uses instead of liquid acid a membrane consisting of a polybenzimidazole (PBI) polymer that is doped with concentrated PA; the latter being responsible for proton conductivity [1,2]. Due to the low vapor pressure of concentrated PA, HT-PEMFCs can be operated conveniently between 150–180 °C without risk of significant losses of PA due to evaporation. By comparison, the ion conductivity of membranes (typically Nafion) used in low temperature (LT) PEMFCs is based on hydronium ions and thus requires liquid water molecules. Consequently, operation temperatures of LT-PEMFCs are limited to below 100 °C. For the same reason, LT-PEMFCs require humidified fuel gas in order to prevent drying out of the membrane on the anode side. The higher operation temperature of HT-PEMFCs leads to a more efficient use of the produced waste heat. Another advantage of HT-PEMFCs is the reduced adsorption strength of strongly adsorbing catalyst poisons as for instance CO owing to elevated operation temperature. Thus, HT-PEMFCs can tolerate lower fuel purity, which makes them suitable even for operation with H_2-rich syngas generated by reforming of for instance natural gas. Although the latter is not a scheme for renewable energy supply, such use might help the marked entry. Indeed, it has been demonstrated that Pt-based HT-PEMFC electrodes at 150 °C can tolerate a CO content of about 5000 ppm without significant reduction of the relative catalyst activity [3]. In LT-PEMFC electrodes operated at 85 °C the relative activity was reduced about 30% by only 20 ppm CO [4].

Despite these principal benefits in terms of convenient operation, increased CO tolerance, and suitability for reformed hydrocarbon fuels, HT-PEMFCs require a significant higher mass

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loading of Pt-based catalysts than LT-PEMFCs in order to achieve a given power output. This is in contrast intuition, which expects lower catalyst loadings due to faster reaction kinetics at elevated temperatures. The principle reason for the poor performance of the electrocatalysts in HT-PEMFCs is not completely understood. In any electrocatalytic reaction, the reaction rate is determined by the number of free active catalyst sites and by the mass transport of reactants and products to and from these active sites. Many studies have shown that the PA is a key factor for the observed lower current densities in HT-PEMFCs, while especially the oxygen reduction reaction (ORR) taking place on the cathode is severely affected by the PA electrolyte. The inhibiting effect of the electrolyte on the ORR activity has been often explained by strong adsorption of PA ions on active catalyst sites [5–9]. We have recently demonstrated using cyclic voltammetry that adding even trace amounts of PA to electrolyte solutions that weakly interact with Pt-catalyst surfaces can lower the ORR catalytic activity by more than one order of magnitude [10]. In another study we have shown by performing potential hold experiments that the apparent ORR diffusion-limited current density decays on a time scale of minutes in PA electrolyte solutions, while in $HClO_4$- and H_2SO_4-based solutions it decreases much less under the same conditions [11]. From the results we concluded that additional effects of reaction inhibition could play a role, which might involve building up of a mass transport limiting barrier at the electrode-electrolyte interface. Aside from processes at the interface, the solubility and diffusivity of dissolved gaseous reactants in the bulk of highly concentrated PA are important parameters to characterize the reactant mass transport in fuel cell electrodes [12–15]. Mass transport of reactant gases in electrode layers of PAFC and PEMFC is generally considered by thin-film models suggesting a surface coverage of catalyst particles or agglomerates with electrolyte films that have bulk properties [9,14–17].

Therefore knowledge of both solubility or concentration (c) and diffusivity (D) of a gas for a given PA concentration and temperature is helpful for investigating the performance inhibition of HT-PEMFCs. Gubbins and Walker used gas chromatography for solubility studies of O_2 at room temperature over the whole PA concentration range; these studies were extended to concentrated PA at temperatures up to 180 °C [18,19]. Their attempts to determine D in a glass diaphragm cell in concentrated PA above 80 °C where unsuccessful due to corrosion issues and the very slow diffusion of O_2 in the concentrated acid. Gan and Chin studied c and D over the whole concentration range at 23 °C [20]. They used a rotating ring disc electrode (RRDE) to obtain D from the “transit time” of the diffusion of O_2 from the disc to the ring, and determined c from the diffusion limited ORR current at the disc. In a number of studies estimates for both c and D are presented at conditions relevant for HT-PEMFC operation: Klinedinst et al. obtained c and D simultaneously from current transients of the ORR on shielded Pt wire electrodes from 100 to 150 °C [21]. Following the concept introduced by Winlove et al. [22], studies on Pt microelectrodes were presented by Scharifker et al. and Gang et al. at temperatures up to 150 °C, and by Essalik et al. up to 100 °C [23–25]. Related to the introduction of the PA-doped PBI membrane, Liu et al. studied O_2 mass transport in PBI-H_3PO_4 blends interfaced with Pt band microelectrodes [26]. The variety of above mentioned studies in pure concentrated PA and PA-doped PBI provide valuable estimates for solubility and diffusivity of O_2 at working conditions of HT-PEMFCs. However, the data contain a significant spread, making correct quantification of O_2 mass transport in HT-PEMFCs difficult [13]. Furthermore, many research efforts are directed to additive-modified PA electrolytes that may improve the ORR for instance via changes in solubility and diffusivity of O_2 or via a reduced specific adsorption [23,27–29]. This draws ongoing interest in solubility and diffusivity data of PA-based electrolytes at elevated temperatures. Methods involving macroelectrodes such as RDE [30] or RRDE [20] have the potential for fast determination of c and D, but they are impeded by the low solubility of O_2 in concentrated PA. In this regard, working in pressurized systems is advantageous [31–34]. As a step towards studying the ORR at realistic conditions in pressurized half-cell setups, in the present study we therefore investigate the oxygen solubility and diffusivity in diluted phosphoric acid electrolyte in a temperature range of 5 to 80 °C. The presented work demonstrates and discusses under which conditions reliable data for these constants can be obtained using rotating disk electrode (RDE). The data are a basis for more complex studies in concentrated PA under pressurized conditions.

2. Experimental

The measurements were performed with a RDE system, which consisted of a rotator EDI101 combined with speed control unit CTV101 (Radiometer Analytical, France). The system was interfaced to an ECi-200 potentiostat operated with the EC4U software package (Nordic Electrochemistry). In the software a calibration was implemented that provides an accuracy of the applied rotation rate of ±1 rpm. As working electrode a homemade polycrystalline-Pt (poly-Pt) RDE tip with geometrical surface area of approx. $0.0314\,cm^2{}_{Pt}$ was used. It was made from a Pt rod of 99.99% purity (MaTeck, Germany) with diameter of 2 mm and a height of 3 mm. Several RDE tips were designed in order to test different material combinations. As main body of a tip we used a cylinder 11 mm in diameter made out of either PEEK or PTFE. Main bodies were made with a 3 mm deep round cavity in the center that served for the insertion of an assembly of Pt rod and a ring of either PTFE or PFA. The rings with inner diam. = 2 mm and outer diam. = 4 mm were cut from PTFE or PFA tubing (Bohlender, Germany). After insertion of the rod-ring-assembly, the RDE tips were polished using first SiC grinding paper of 15 and 5 μm grain size and thereafter de-agglomerated alpha alumina suspensions of 1 and 0.3 μm grain size (Struers, Denmark) on a polishing felt (Struers) wetted with water. After polishing the tips were cleaned ultrasonically first in isopropanol and finally in ultra-pure water three times for at least 10 minutes. A gold plated spring contact (PTR Messtechnik, Germany) was used for providing electrical contact between Pt electrode and stainless steel RDE shaft.

Two different electrochemical cells were used. For measurements at a fixed temperature of 25 °C, the electrochemical cell was based on a 100 ml Pyrex glass laboratory flask with a custom made lid made of PTFE. In order to support the RDE, the lid has conically tapered joint. Furthermore, it has several holes for inserting counter electrode (CE), reference electrode (RE) and for gas supply. CE and RE were built of Pt wire 0.6 mm in diameter and Pt gauze of 20×20 mm (99.9%, wire diam. = 0.06 mm, 1024 mesh cm^{-2}) purchased from MaTeck, Germany. The Pt mesh RE was placed in a glass capillary which was purged with a small quantity of H_2 gas in order to obtain the potential of the reversible hydrogen electrode (RHE) as reference potential for the WE. Therefore all potentials are given with respect to the potential of RHE. The capillary had an opening of approx. 0.5 mm in diameter and resembled a Haber-Luggin capillary. However, in order to achieve an undisturbed flow pattern towards the WE, the opening of the capillary was placed in the bulk of the cell instead of bringing it as close as possible to the WE surface. The volume of electrolyte in the cell was 70 ml. In order to avoid altering the concentration of the PA solutions during the measurements, all gases used except H_2 for the RHE were humidified before entering the cell. For this, the gases were guided through a gas bubbler containing a volume of approx. 50 ml of electrolyte of the same concentration as used during measurements. The PA solutions were kept at 25 °C by