Short communication

Oxygen permeability of cast ionomer films from chronoamperometry on microelectrodes

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HIGHLIGHTS

- First correct determination of oxygen permeability of cast ionomer from chronoamperometry on microelectrodes.
- More rigorous data analysis than in previous studies on oxygen permeability of polymer membranes.
- Factors responsible for changes of oxygen diffusion geometry through thin ionomer films identified.

ARTICLE INFO

ABSTRACT

The paper presents a method for determination of diffusion coefficient and solubility of oxygen in cast polymer electrolyte from chronoamperometry of oxygen on polymer electrolyte coated platinum disk ultramicroelectrodes. The approach is based on numerical fitting of measured currents to the known but not previously used for polymer electrolytes equation derived by Shoup and Szabo. The method was applied to cast films of a novel polymer electrolyte 6F-40. As opposed to Nafion®, cast 6F-40 films do not undergo interfacial restructuring, i.e., they retain their original morphology under selected temperature and humidity conditions, which allows for accurate determination of both parameters from measurements for a range of electrode radii and film thicknesses. It is demonstrated that the Shoup and Szabo equation satisfactorily describes measured current transients for shorter oxygen reduction times, *i.e.*, when the diffusion field in the thin polymer film can be regarded as semiinfinite. The accuracy of the diffusion coefficient and solubility determinations was not measurably affected by the product water and the observed systematic changes of the fit quality in various time domains were attributed to approximate character of the fitting equation.

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1. Introduction

Effective transport of oxygen to catalyst particles in polymer electrolyte fuel cells (PEFCs) is one of the key factors determining performance of the PEFC cathode. Therefore, oxygen permeabilities of Nafion® and alternative polymer electrolytes have been determined under various experimental conditions in numerous studies [1—10]. In many of those studies, chronoamperometry of the transport controlled oxygen reduction reaction (ORR) was measured in solid state electrochemical cells, where a disk shaped platinum ultramicroelectrode (UME) was pressed against a polymer electrolyte membrane in contact with humidified oxygen [9,10]. Assuming that the number of electrons participating in ORR was four, the method allowed for simultaneous determination of

oxygen solubility (C_0) and diffusion coefficient (D), using the so called modified Cottrell equation [11]. However, the oxygen transport characteristics determined for preformed membranes [9,10] are expected to be different than those in the PEFC catalyst binders employing the same ionomer, as membrane manufacturing affects the polymer morphology [1,12]. On the other hand, studies utilizing solid state cells with Pt UMEs in contact with cast Nafion® films, whose morphology more closely resembles ionomer morphology in the catalyst layer, demonstrated interfacial restructuring of the polymer at the interface with smooth platinum surfaces [13—16]. The phenomenon results in the hydrophobic component of the ionomer being pushed out to its interface with bare Pt. Under such conditions, the apparent rate of ORR is reduced to such extent that the reduction current decreases even in the potential range where the reaction rate should be controlled exclusively by transport [13—16]. In consequence, the accuracy of a chronoamperometric determination of oxygen permeability is expected to progressively deteriorate with the reduction time. In this

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paper, we demonstrate a successful determination of the diffusion coefficient and solubility of oxygen in cast films of a novel, hydrocarbon based, proton-conducting polymer (6F-40) [17]. Cast films of 6F-40 retain their original morphology during ORR in a narrow range of temperature and humidity conditions, which makes it possible to measure transport controlled ORR currents unaffected by interfacial restructuring. In the data analysis, we used Shoup and Szabo equation [18], which offers a better current approximation than the modified Cottrell equation [11].

2. Experimental

The working electrode was either a 100 μm or a 50 μm diameter platinum microdisk electrode (Bioanalytical Systems). Before use, the microelectrode was polished with 0.25 μm diamond paste (Buehler) and 0.05 μm alumina (Buehler) and sonicated in deionized water (Millipore). Following multiple potential cycling between 0 V and 1.4 V vs. a hydrogen electrode (6% H_2 in Ar) in 0.5 mol dm^3 H_2SO_4, which resulted in the clean Pt surface, the microelectrode in the reduced state was removed from the solution, promptly rinsed with deionized water (Millipore) and the excess of water was removed with a stream of ultrahigh purity argon.

To recast the ionomer film, the electrode was held with the tip pointing up and a small volume of homemade 5% suspension of 6F-40 was deposited on the electrode with a micropipette. The electrode was then quickly turned and placed in a small volume ($\sim$5 cm^3) chamber filled with dry, ultrahigh purity Ar. Such a procedure guaranteed slow evaporation of the solvent and consequently a smooth film with a uniform thickness in its central portion, where the microdisk was located. The film thickness was measured by profilometry of a sample prepared in an identical way using an electrode that was not used in electrochemical experiments [14,15].

After the film dried out, the electrode was removed from the chamber and ribbons made of Nafion® 117 and of Pt were placed along the opposite sides of the glass body of the electrode. The ribbons were then secured with a Teflon tape, and electrolytic contacts between them and the film were made using small quantities of 6F-40 solution. In the minicell thus produced, the platinum ribbon served as a counter electrode and the Nafion® ribbon acted as an electrolytic bridge between the external reference electrode (6% H_2 in Ar/0.5 M H_2SO_4, E = 39 mV vs. RHE at sea level and 25 °C) and the working electrode (Fig. 1). Subsequently, the minicell was connected to the reference electrode and placed in a controlled humidity chamber (Fig. 1). In order to prevent gas exchange between the reference electrode and the controlled humidity chamber, the Nafion® ribbon passing through in the wall of the reference electrode tube was tightly covered with several layers of Teflon tape (Fig. 1). After that, film was cured for 24 h in argon at the desired temperature and humidity. Lithium chloride solutions (Fisher) of various concentrations were used to control the relative humidity during the film equilibration and the measurements. In order to attain the desired relative humidity (RH), the gas (argon or oxygen) was slowly passed through two large bubblers filled with a LiCl solution of the desired concentration before it entered the controlled humidity chamber partially filled with identical LiCl solution (Fig. 1). During the equilibration and measurements, the bubblers and the controlled humidity chamber were immersed in a controlled temperature water bath.

The electrochemical measurements were carried out with an EG&G PAR Model 283 potentiostat. Before the experiments, the electrode potential was cycled at 50 mV s^{-1} between 0 V and +1.4 V until a stable voltammogram was obtained. In order to provide a consistent electrode pretreatment and a clean Pt surface for every
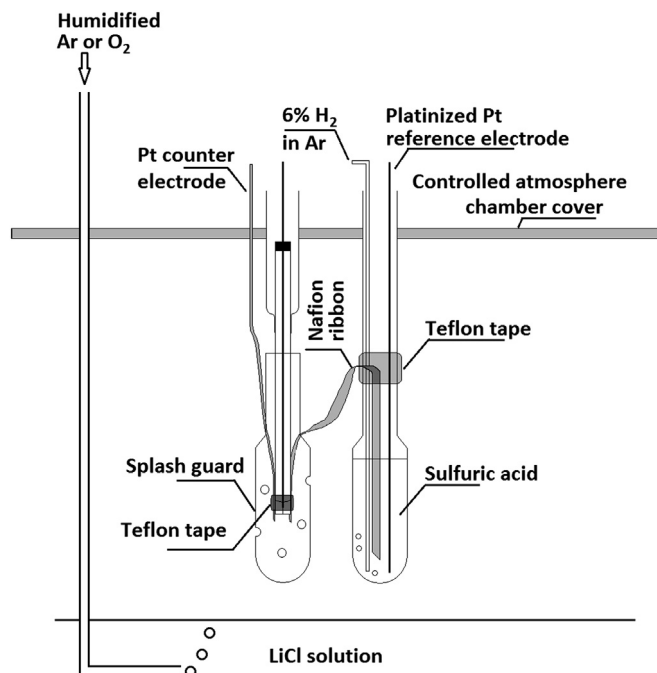

Fig. 1. Schematic of the electrochemical cell applied in the study.

experiment, the microelectrode was held for 10 s at 1.4 V before a cathodic potential step or voltammetric scan was applied.

3. Results and discussion

The top part of Fig. 2 shows a background corrected voltammogram of pure oxygen recorded at 60% relative humidity and 20 °C for a 100 μm Pt disk coated with a 26.5 μm thick film of 6F-40. Well-defined current plateaus that correspond to a transport controlled ORR can be seen in the forward and reverse scans of the voltammogram. The plateaus overlap at potentials ≤0.3 V, which indicates that the ORR is transport controlled in this potential range. Under the identical experimental conditions, a similar experiment for Nafion resulted in a voltammogram with a significantly narrower potential range, where the limiting currents in forward and reverse scans overlapped [14]. Non-existent or short current plateaus in oxygen voltammetry on ionomer-coated microelectrodes are demonstrated signs of ionomer restructuring [14]. The bottom portion of Fig. 2 shows plots of background corrected currents for transport controlled (0.1 V) ORR on 6F-40 coated electrodes at 60% relative humidity recorded under various experimental conditions and plotted versus the inverse square root of time. Irrespective of the film thickness (curves 1 and 3), size of the electrode (curves 1 and 5) and temperature (curves 4 and 5), the plots are essentially linear at shorter times of electrolysis (higher $t^{-1/2}$), whereas the current becomes essentially time independent at longer times. The approximately linear i vs. $t^{-1/2}$ dependence at shorter electrolysis times is consistent with the Shoup and Szabo equation [18] for a transport controlled reaction on an inlaid microdisk (semiinfinite diffusion field):

$$i = i_{ss}\left(0.7854 + 0.8862\tau^{-1/2} + 0.2146 \exp\left(-0.7823\tau^{-1/2}\right)\right)$$

(1)

where i_{ss} is the steady state current corresponding to infinite reduction time (t) and τ is a dimensionless time variable equal to