



Mass Transport and Oxygen Reduction Kinetics at an Anion Exchange Membrane Interface: Microelectrode Studies on Effect of Carbonate Exchange

Iromie Gunasekara,* Myoungseok Lee, Daniel Abbott, and Sanjeev Mukerjee^z

Department of Chemistry and Chemical Biology, Northeastern University Center for Renewable Energy Technology, Northeastern University, Boston, Massachusetts 02115, USA

A Pt micro-electrode investigation conducted on a commercial anion exchange (AEM) membrane (Tokuyama, A-201) shows rather close kinetics for ORR with and without carbonate exchange as well as with a perfluorinated proton exchange membrane analog such as Nafion. A resolution of the mass transport into constituent components, diffusion coefficient and solubility shows that the biggest contribution toward lower overall permeability in AEM when exchanged with CO_3^{2-} is the diffusion coefficient, solubility remaining unaffected. These results show remarkable agreement with polarization corrected fuel cell data, thus enabling a method to better resolve interfacial performance of an AEM fuel cell.

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Development of proton exchange membrane fuel cells, have to be tempered with the cost, a significant portion of which is due to the so called 'stability criterion' restricting the choice to Pt and Pt alloy materials. Fuel cells operating in alkaline media have potential advantage of facile kinetics of oxygen reduction reaction on non-precious group metals and stability at high pH values. In addition, the hydrodynamics of alkaline membrane fuel cells is potentially beneficial considering the problems associated with water management in a conventional PEM fuel cell. Further, highly stable PTFE based membranes are not required under alkaline conditions as the membranes are less prone to attack by peroxide ions.

Even though AEMFCs alleviate most of the hurdles associated with PEM fuel cells, state of art performance of H_2 /air does not exceed half of the performance shown by H_2 fed PEM fuel cells using Pt based catalysts (compare 700 mW cm^{-2} for PEMFCs¹ at 0.65 V (80°C, 100%RH) with $\sim 40 \text{ mW cm}^{-2}$ for AEMFCs² at 0.65 Volts (50°C, 85%RH).² The major concern under atmospheric air feed is carbonate exchange of the hydroxyl ions in the polyelectrolyte due to their complete conversion to carbonate and bicarbonate ions upon exposure.³⁻⁵ In such instances only HCO_3^- and CO_3^{2-} are responsible for ionic conduction.⁶ Under 100% RH conditions, Donnan exclusion of protons within the membrane and ionomer results in a higher pH in the membrane interstitial solution, than the pH in the external solution. In other words the membrane and ionomer should be enriched in carbonate ions when exposed to normal air. Prior work⁷ has shown that a significant portion of the bicarbonate ions dissociate into either carbonates or carbonic acid due to the relatively weak basicity of quaternary ammonium ion exchange sites in commercial AEMs (this work). Grew et al.⁸ has studied the temperature dependent carbonate/bicarbonate ion distributions and has rejected the misconception that air equilibrated AEMs are in HCO_3^- form.

It is well known that conductivities of carbonate ions in aqueous solutions are lower than hydroxyl ions due to larger hydration spheres arising from the size and surface charge densities.⁹ As reported earlier, relative decrease in ionic conductivity as a function of exchange with carbonate and bicarbonate ions is low.^{10,11} Permeation of reactants in the ionomer and membrane thus play an important role in determining the onset of mass transport and hence the power density of the AEM fuel cells. Details of interfacial kinetics and mass transport of dissolved oxygen and the quantitative effect on the performance by carbonate exchange is relatively unknown. This communication provides for the first time an insight on the relative magnitudes of kinetic as well as mass transport of oxygen molecules in AEM with and without carbonate exchange.

Well known quaternized anion exchange membrane ((Tokuyama A201, Tokuyama Corp., Tsukuba, Japan) was used in this study in con-

junction with a solid state electrochemical cell incorporating a micro-electrode, described in detail elsewhere.^{12,13} The parameters obtained were free from effects typically encountered in liquid electrolytes such as hydroxide ion adsorption effects and presence of mobile cations. Conventional ORR kinetics reported on rotating disk electrodes in aqueous electrolytes greatly deviate from the kinetics of the membrane electrode interface.¹⁴ This paper for the first time resolves the kinetics from the mass transport contributions (diffusion coefficient and solubility) of oxygen reduction reaction. Results of this work are used to understand polarization losses at typical fuel cell interface.

Experimental

Membranes.— Tokuyama-A201 membranes (Tokuyama Corp., Tsukuba, Japan) were treated with 1 M KOH, rinsed and stored in CO_2 free water. Membranes in the hydroxide form were exchanged to carbonate form by treating with 1 M K_2CO_3 which were then rinsed and stored in milli-q water overnight to leach excess carbonate ions.

Electrodes.— Solid state electrochemical cell was used with dynamic hydrogen electrode (DHE) as the reference. The detailed design and construction of this cell is reported earlier in conjunction with similar measurements in proton exchange membranes.^{12,13} The working electrode was a 100 μm Pt micro-disk electrode (Bioanalytical Systems), a 1.6 mm diameter Pt disk was used as a counter electrode. All three electrodes were cleaned using a series of diamond polishes starting with 15 μm , and followed with 3 μm and 1 μm respectively, sonicated in milli-q water for 10 minutes. The DHE was subsequently platinized prior to use.

Electrochemical techniques.— Voltammetric measurements were taken using a computer controlled potentiostat/galvanostat (Autolab, model PGSTAT30) at room temperature and at 1 atm pressure. Measurements of carbonate free membranes were carried out in CO_2 free conditions enabled by an Ar filled glove bag. Potentials were scanned from 0 V to 1.3 V in nitrogen at 100 mV s^{-1} , to clean the electrode surface prior to taking readings. Slow sweep voltammograms were recorded at 2 mV s^{-1} in oxygen. All potentials were corrected to the reversible hydrogen electrode (RHE) scale before analysis. The current at a microelectrode is given by modified Cottrell equation,

$$I = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} + n\pi FDCr \quad [1]$$

where n is the number of electrons per reduction of oxygen molecule. F is the Faraday constant, A is the geometric area and r is the radius of the electrode. D and C are diffusion coefficient and solubility of oxygen in AEM. Chronoamperometric measurements were carried out by conditioning the electrode potential at 1.0 V for 10 s and stepping down to 0.4 V for 20 s with respect to RHE. Prior to this the cyclic

*Electrochemical Society Student Member.

^zE-mail: s.mukerjee@neu.edu