Proton Transport in Ionomer-free Regions of Polymer Electrolyte Fuel Cells and Implications for Oxygen Reduction Reaction

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In polymer electrolyte fuel cells (PEFCs) catalyst layers have to accommodate electron, oxygen and proton delivery to the electracatlyst site. Proton conduction is achieved by adding ionomer solution into the catalyst ink. Due to size exclusion and wetting properties ionomer is not present in micro-pores of carbon particles and sometimes in meso-pores too. The question arises what is the mechanism of proton delivery to the electrocatalyst site, which is not in contact with ionomer. Additionally, the dependency of rate determining step of oxygen reduction reaction on protons needs to be revisited. We present here an overview of recent advances in understanding proton transport and reactivity in ionomer-free domains of the catalyst layer of the PEFCs and describe how non-monotonic metal charging enhances local proton conductivity.

Keywords: ionic conductivity; oxygen reduction reaction; ionomer-free; catalyst layers; fuel-cells.

1. Introduction

Conventional catalyst layers in polymer electrolyte fuel cells (PEFCs) are composed of nano-particles of electrocatalyst (such as platinum (Pt)) dispersed onto a carbon support, which is bound most commonly by perfluorosulfonated ionomer (PFSI), such as Nafion [1, 2]. Recent reviews provide a detailed description of challenges in optimizing catalyst layer formulation [3, 4]. Figure 1 shows a schematic of carbon agglomerate covered by ionomer that allows effective proton conduction. Ionomer size-exclusion results in ionomer-free micro-pores (< 2 nm) within the porous carbon support. Accessing Pt within these micro-pores with protons and oxygen might be difficult. Porous carbons such as Ketjenblack have high surface area (500 – 2000 m^2/g), good Pt dispersion and high electrochemical surface area (ECSA), enabling 2-3 times higher mass activities compared to solid carbons [5-7]. Large portion of Pt nano-particles reside within micro-pores of the porous carbon particles [8-10]. A team led by General Motors [6] considers pros and cons of porous vs. solid carbons (Vulcan, acetylene black), where major concern is ionomer directly contacting and poisoning Pt surface. [11] They postulate that the ideal carbon support hosts Pt within its micro-pores without directly interfacing with ionomer but allowing protons and oxygen delivery. Several studies have shown that the ECSA of Pt supported on high surface area carbons strongly depends on relative humidity (RH), indicating that the condensed water pathways are necessary to detect Pt [10, 12]. Currently, the mechanisms for ion transport in ionomer-free portions of the catalyst layer are not well-understood. The migration is possible if surface of Pt is negatively charged, this implies non-monotonic charging behavior away from potential of zero charge (pzc) that is ~0.23 V for Pt. [13, 14] Recent studies measured bulk ionic conductivity of humidified Pt or carbon supports and have shown both RH and applied potential dependency of ion transport processes [15-19].

Figure 1b-d summarized findings from the PEFCs ionic conductivity studies. In pioneering work Thompson et al. [16] have shown that ionic conductivity in Pt black electrode bound by PTFE is 2-3 orders higher than that of deionized (DI) water but it is 1-1.5 orders of magnitude lower than that of conventional catalyst layer with ionomer. Huang et al. [17] infiltrated micro-pores of the catalyst layer with protic ionic liquids and compared its ionic conductivity to conventional catalyst layer and that with combined ionic liquids and Nafion. As shown by Figure

1c catalyst layer with combined ionic liquid and Nafion showed the lowest ionic resistance. This might be due to high ionic strength of ionic liquid increasing proton mobility. Modestov et al. [18] showed similar ionic conductivity trend for porous carbon support and that with electrocatalyst. An order of magnitude decrease in ionic conductivity was observed, when potential increased from 0.1 to 1.1 V (Figure 1d). This decrease in conductivity was attributed to positive surface charging of carbon, which is away from its pzc at around 0 – 0.3 V. Hu et al. [19] confirmed the findings for solid carbon support. Additionally, studies reported current ignition at low potentials, corresponding to high ionic conductivity region but also to higher current density and water generation rates [20, 21]. In this review we provide an overview of recent discoveries related to ion transport in ionomer-free environments and how these findings effect ORR in PEFCs.

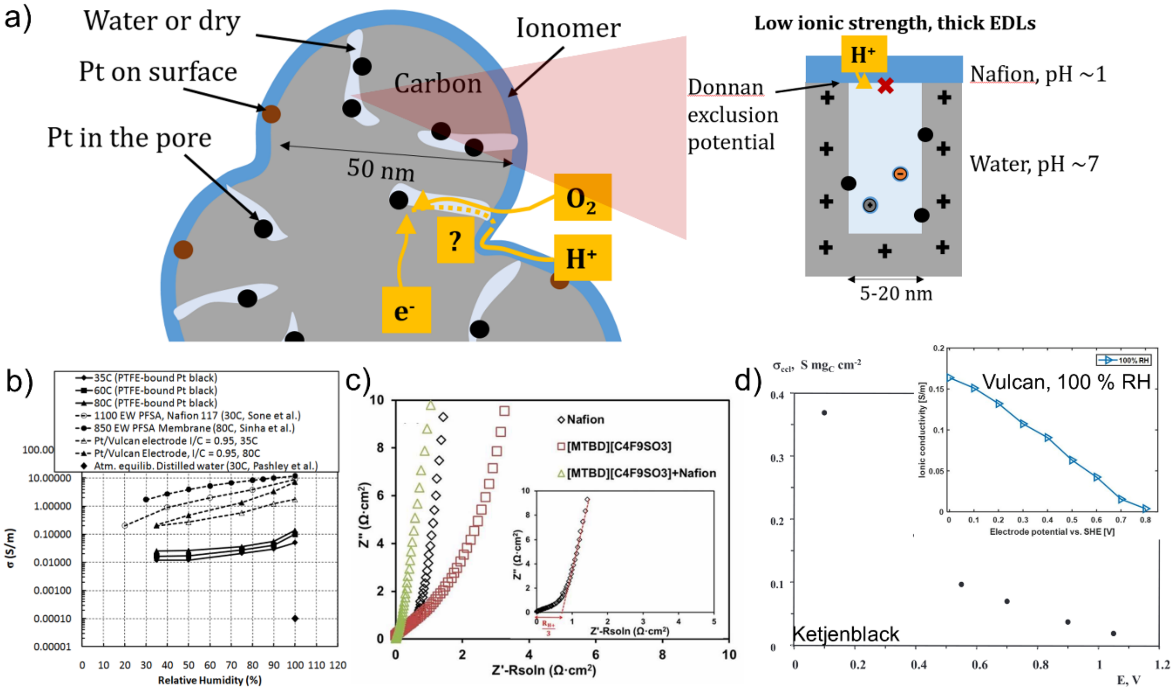


Figure 1. a) Schematic of high surface area carbon agglomerate in PEFCs with zoom-in view of meso-pore, b) ionic conductivity as a function of RH from Thompson et al. [16] , c) increase in ionic conductivity with meso- and micro-pores filled by ionic liquids from Huang et al [17] and d) proton conductivity as a function of applied potential for Ketjenblack as reported by Modestov et al [18], where inset shows similar trend for Vulcan carbon from Hu et al.[19]

2. Role of protons in oxygen reduction reaction

This section reviews the dependency of the rate-determining step (RDS) of the ORR on Pt or other alloy electrocatalysts supported on carbonaceous materials on the concentration (availability) of protons. Rotating disc electrode (RDE) experiments are commonly used to assess electrocatalyst activity towards ORR, where 0.1 – 0.5 M acid is used. Under such conditions protons are abundant and ionic conductivity of supporting electrolyte is high. Within the catalyst layer protons transport from anode and conductivity of water-filled pores is several orders of magnitude lower than that of the RDE environment (Figure 1). Difficulty in translating RDE electrocatalyst activities into catalyst layer activities is one of the major issues in the PEFCs community [22-24]. Yeager [25] was the first one to show no kinetic isotope effect (KIE) on Pt electrocatalyst in deuterated phosphoric acid. This is indicative that protons do not participate in the ORR RDS. More recently, Gewirth's group [26] have shown similar results for Pt at three pH values in deuterated sulfuric acid. Ion poisoning of Pt surface cannot be neglected in phosphoric and sulfuric acids, ideally these KIE studies should be conducted in perchloric acid. These are the only two studies that probed KIE on Pt surfaces. Additional studies have looked into ORR on Pt-group metal free (PGM-free) electrocatalysts and found that KIE is larger than 3 [27], on the other hand for metal-free catalysts Sakaushi et al. have shown no KIE in acid for ORR on carbon-based electrocatalysts [28].

It has been shown as early as by Damjanovic works that at low current density the proton reaction order is 3/2 [29]:

$$i = knF[H^+]^{3/2} p_{O_2} exp\left[\frac{-FV}{RT}\right] \tag{1}$$

The 3/2 reaction order is due to reaction activation energy being function of pH also. Figure 2a summarizes the Tafel slopes and ORR potential dependencies on pH in both acid and alkaline electrolytes. This dependency on pH translates to a large 90 mV potential drop for a change in pH by a unit in low current-density regime. Depending on high or low-surface area carbon support Pt electrocatalyst can be buried within the carbon particles without direct access to Nafion ionomer. In such scenarios local pH will be lower [15], which can result in lower potential and decrease in performance. Most of the mechanistic models for the ORR neglect protons terms in the kinetic equations. [30, 31]. Zenyuk and Litster have shown significant ORR dependencies on the local proton concentration in their model. [15] More recently, Eikerling's group has shown that ORR rates can be significantly enhanced at high potentials by proton availability (Figure 2b). [32]

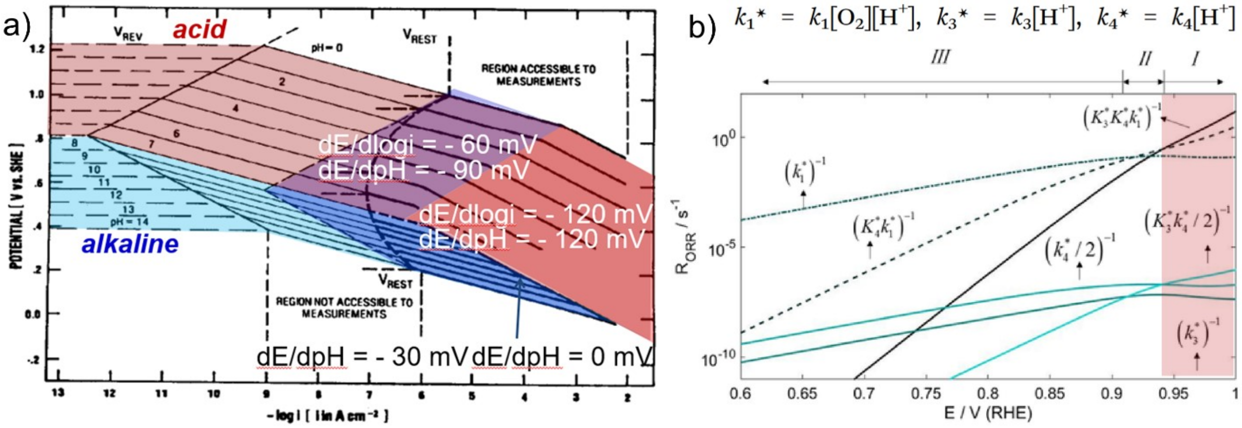
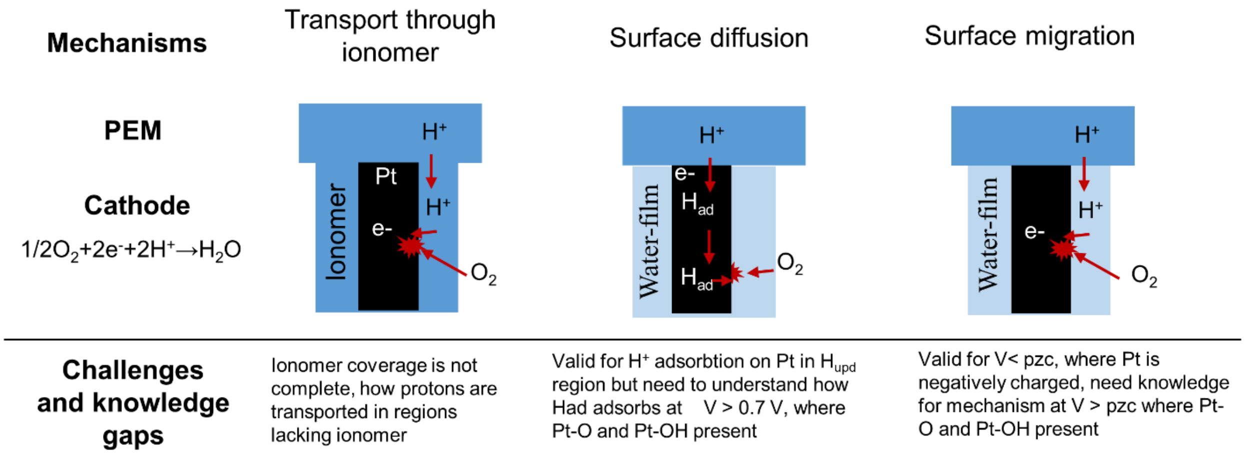


Figure 2. a) A summary plot for ORR in acid and alkaline environments from Sepa et al. [29] and b) a modeling prediction for the ORR reaction rate as a function of applied potential from Huang et al. [32].

3. Mechanisms for proton transport in ionomer-free films

Understanding ion transport in water-filled domains of catalyst layer can help with the design considerations. Several experimental and modeling studies propose two transport mechanisms: 1) H_{ad} surface diffusion [33-37] and 2) water-mediated proton surface migration [38, 39]. Figure 3 compares proton transport in ionomer-filled regions to those of water-filled. The first mechanism has been primarily supported by select few studies with the cyclic voltammetry electrochemical results. The second mechanism was supported with modeling studies [32, 38, 40] and more recently indirectly deduced through experimental data [14].

Ion transport mechanisms primarily depend on electrocatalyst surface conditions, which are dictated by applied potential and thermal conditions. Mechanism one is the most favorable for a potential range $V < 0.4$ (V vs. SHE) where the electrode is covered with adsorbed hydrogen. Both, Pt supported on carbon and Pt show similar H_{upd} regions when in contact with Nafion, therefore the first step of hydrogen adsorption at the interface between electrode and PEM is likely to happen on both [33, 34]. Whereas, the second step, where H_{ad} diffuses along the surface of electrocatalyst or carbon support depends strongly on whether electrode has continuous or dispersed Pt particles. For electrocatalyst with dispersed Pt particles hydrogen "spillover" happens. In the spillover process, hydrogen adsorbs on electrochemically active catalyst cite (Pt) and then diffuses onto the surface of the inert support, which does not adsorb hydrogen on its own [35, 41-44]. Pt particles that are located away from Nafion can be utilized in electrochemical reaction and spillover mechanism can contribute significantly to the overall ionic conductivity. The second mechanism requires electrostatic interaction between electrocatalyst and ion. For protons to migrate along the surface, Pt (or support) should carry negative charge, which is only possible in a region of applied potential being lower than the metal's pzc ($V < pzc$), if monotonic charging of Pt is assumed. It is possible for migration to occur at $V > pzc$ along the surface covered with Pt-O and Pt-OH, where surface oxides act as dipoles with O and OH surface groups having negative charge. The next section describes this phenomena in more detail.



Ionomer coverage is not complete, how protons are transported in regions lacking ionomer

Valid for H^+ adsorbtion on Pt in H_{upd} region but need to understand how Had adsorbs at V > 0.7 V, where Pt-O and Pt-OH present

Valid for V< pzc, where Pt is negatively charged, need knowledge for mechanism at V > pzc where Pt-O and Pt-OH present

Figure 3. Proposed mechanisms of proton transport in ionomer-filled and ionomer-free meso-pores. Surface diffusion is compared to surface migration.

4. Non-monotonic charging of Pt

The potential of zero free charge (pzfc), ϕ_{pzfc} is defined as potential at which electrode carries zero charge, where the surface free charge density, σ_{free} can be related to the metal potential, ϕ_m, and pzfc in a linear fashion:

$$\sigma_{free} = C_{dl}(\phi_m - \phi_{pzfc})$$

Essentially, the electrode obtains positive charge above pzfc and negative charge if the metal potential is below pzfc. This behavior is monotonic. The pzfc considers the electronic charge on the metal, whereas the potential of zero total charge (pztc) takes into account additional charge due to adsorption [45-47]. The potential of maximum entropy (pme) of double-layer formation is close in value to pzfc. The pme is obtained with laser-pulse experiments, where water molecules orientation at the interface is tracked and a potential at which water molecules turn from oxygen-toward-the-metal orientation to hydrogen-toward-the-metal orientation is defined as pme [13]. Water molecules that form a dipole layer are affected by the free charge of metal because of electric field, however, specifically adsorbed species will also impact this interaction and hence the pme also shows correlation to the pztc. The total charge of the electrode is related to its free charge via:

$$Q = \sigma_{free} - F\Gamma_H + F\Gamma_{OH}$$

where Γ_H and Γ_{OH} are the thermodynamic excesses of hydrogen and hydroxide, respectively. For Pt (111) the pzfc, pztc and pme are all close to each other, the pzcs being close due to double-layer region, where there is no species adsorption. It was found that the pzfc and pme are independent of pH in double-layer region, however, at lower potential (in Had region) and higher potential (OH-adsorption region) the pzfc strongly depends on pH on SHE-scale, where the shift is 60 mV/dec. [13] Frumkin and co-authors [45] with a radiotracer experiments reported electrode charge reversal from 0.5 to 0.8 V, acquiring positive total charge, and changing to negative again at higher potentials. Feliu and co-authors confirmed this observation [14], showing pH independence of the secondary pztc of Pt. Since Pt is covered by oxides in this high potential region, it has its own interfacial characteristics. Eikerling's group [48] proposed a modification to classic Guoy-Chapman-Stern electric double layer (EDL) model to account for water dipoles and surface oxides to shield the electric field, showing that majority of potential drop can be shielded by both dipoles and surface oxides, as oppose to classic treatment where ions shield the electric field at the EDLs. Kongkanand and co-authors [9] are the first ones to apply CO-displacement technique to study Pt-ionomer interaction in conventional catalyst layers. They have confirmed pztc at 0.26 V and observed the charging behavior up to 0.5 V. Due to CO oxidation reaction at higher potentials, CO cannot be used as a pztc probe. Feliu and co-authors reported a variety of alternative probes sensitive in that potential region [49, 50].

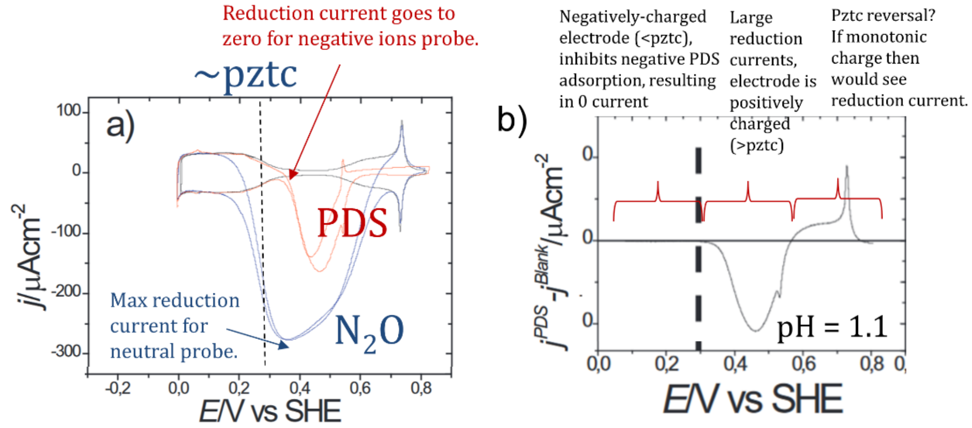


Figure 4. Feliu's group investigation of peroxodisulfate (PDS) and N_2O reduction on Pt. [14]. Using subtraction technique they were able to observe an oxidation current at potentials higher than 0.5 V, indicating a possibility of the Pt pztc reversal.

5. Conclusions and Future Outlook

Recent studies on non-monotonic Pt charging support the hypothesis of proton migration as primary transport mechanism for proton conduction in ionomer-free domains of catalyst layer. Going forward more studies will be conducted to validate the secondary pztc due to formation of oxide layer on Pt surface and mechanistic studies and models are needed to confirm and explain its impact on the ORR. The efforts to shift the onset for Pt oxides formation to free Pt surface for ORR [17, 51-54] can have effect on the second pztc and proton conductivity. Strong dependency of the ECSA on relative humidity for porous carbons indicates that to access Pt in domains without ionomer condensed water is needed. This brings a concern of PEFCs meeting robustness criteria. Decrease in ionic conductivity for carbon blacks with applied potentials confirms that electric field is one of the driving forces for proton transport. Understanding carbon blacks surface groups chemistry and their dependency on pH can significantly enhance understanding of proton transport in carbon-supported Pt catalyst layers.

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