A Microelectrode Study of Interfacial Reactions at the Platinum-Alkaline Polymer Interface

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dedicated to the memory of our colleague, Richard J. Bailey

Hydrogen oxidation (HOR) and oxygen reduction (ORR) reactions at the platinum/alkaline ionomer interface were investigated using two different alkaline polymer electrolytes, i.e., benzyl-trimethyl ammonium tethered poly(phenylene) (ATM-PP) and phenylpentamethyl guanidinium tethered perfluorinated polymer (M-Nafion-FA-TMG). Substantial inhibition of HOR was taking place at the platinum-ATM-PP interface due to the possible cationic group adsorption of ATM-PP, whereas the reaction was virtually unaffected at the platinum-M-Nafion-FA-TMG interface after high anodic potential preconditioning. Moreover, the apparent ORR activity of platinum coated with M-Nafion-FA-TMG was found higher than that of 0.1 M tetra methyl guanidinium solution. In addition, the oxygen permeability of M-Nafion-FA-TMG was found to be ∼2.5 times higher than that of ATM-PP. The above properties of the perfluorinated polymer make it a very promising ionomeric binder for the use in both anode and cathode of alkaline membrane fuel cells.

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Manuscript submitted November 6, 2014; revised manuscript received February 9, 2015. Published February 24, 2015. This was Paper 630 presented at the Orlando, Florida, Meeting of the Society, May 11–15, 2014.

Alkaline membrane fuel cells (AMFCs) have drawn tremendous attention because they have the potential to convert hydrogen fuel to electricity without using precious metal catalysts in the electrodes.1,2 However, the current performances of AMFCs using non-precious or even precious metal catalysts are inferior to those of proton exchange membrane fuel cell (PEMFC) counterparts.3 The inferior performance of AMFCs has been explained by the low hydroxide mobility in anion exchange membranes,4,5 carbonate/bicarbonate formation,6–8 and also slow hydrogen oxidation reaction (HOR) kinetics,9,10 and poor water management.11–15 The differences in performance between AMFCs and PEMFCs are also largely derived from the polymer electrolytes employed in the electrodes that provide different environments for electrochemical reactions and material diffusion. The effects of cation-tethered alkaline polymer electrolytes on AMFC performance have been investigated by several research groups. Varcoe et al. first used a hydroxide conducting ionomer in preparation of alkaline metal-cation-free AMFC electrodes.16 There was a substantial increase in the peak power density of AMFCs (55 vs. 1.6 mW cm−2) by adding quaternized poly(vinylbenzyl chloride) to the catalyst layers and further improved AMFC performance was reported later using better ionomer dispersion technology,17 i.e., the peak power density of 185 mW cm−2. However, the improved AMFC performance was still inferior to the state-of-the-art PEMFC performance. They suggested that relatively low gas permeation by ionomer binder may be the reason for the inferior performance. Researchers from Tokuyama Corporation reported a series of hydroxide conducting ionomers for AMFC applications.16,17 They found that the peak power density of the AMFC performance increased from 22 mW cm−2 to 296 mW cm−2, as the ion exchange capacity of their hydrocarbon ionomers increased from 0.7 to 1.8 meq. g−1. They suggested the ionic conductivity of the ionomer is the major factor contributing to the performance improvement but other factors, e.g., the catalyst electrochemical surface area may have played a role as well. Recently, we have prepared hydroxide conducting perfluorinated and poly(phenylene) polymer electrolytes to evaluate the ionomer performance in use of electrode binders.18 The peak power density of AMFC measured using the perfluorinated ionomeric binder in the catalyst layers was 577 mW cm−2 which was 1.7 times higher than that when using the poly(phenylene) ionomer. This was a somewhat surprising result considering that the hydroxide conductivity of the poly(phenylene) ionomer was about four times higher than that of the perfluorinated ionomer. The finding suggests that the hydroxide conductivity of ionomeric binders in the AMFC electrodes may not be the major factor affecting the electrode performance, although the reason for the superior performance using the perfluorinated ionomer remains a question.

Besides the issues with the hydroxide conduction and gas permeation of hydroxide conducting ionomers, electrochemical interferences by cationic functional group have been recognized as a possible factor responsible for the inferior AMFC performance. Unlu et al. compared the cyclic voltammograms on polycrystalline smooth Pt electrodes in 0.1 M NaOH and tetramethyl ammonium hydroxide (TMAOH) electrolytes.19 They observed that the anodic hydrogen desorption charge from Pt in the voltammograms recorded for TMAOH solutions was 2.6 times lower than that for NaOH solutions due to the specific adsorption of quaternary ammonium ions on the Pt surface. The adsorption was found detrimental to methanol oxidation reaction. Ong et al. reported that electrolyte cations containing phenyl groups had a stronger inhibitory effect on oxygen reduction reaction on Pt than those containing exclusively aliphatic groups, i.e., tetramethyl ammonium (TMA+) ions.20 In spite of their importance, the above mentioned studies focused exclusively on the effects of the cations in liquid electrolytes whose interface behavior in contact with the catalyst may differ from that of polymer electrolytes containing similar cationic groups tethered to the polymer backbone.

In this research, we investigate the effect of two significantly different anion exchange polymer electrolytes, i.e., guanidinium functionalized perfluorinated ionomer (M-Nafion-FA-TMG) and benzyl trimethyl ammonium functionalized polyaromatic ionomer (ATM-PP) on hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) of Pt. In order to decouple the effects of the respective cationic groups from those of the polymer backbone, the HOR and ORR voltammograms of Pt were studied in presence of the ionomers and also liquid electrolytes containing analogous cationic groups, i.e., tetramethyl guanidinium (TMG) and benzyl trimethyl ammonium hydroxide (BTMAOH). Well-established microelectrode mini-cell set-up21,22 was used for the electrochemical measurements of the HOR and ORR activities of Pt at the interfaces as well as O2 permeability of the two ionomers.
Experimental

Material preparation.— 1,1,3,3-tetramethyl guanidine (TMG, Acros, 99%), tetramethyl ammonium hydroxide (TMAOH, TCI, 40% in water) and benzyl trimethyl ammonium hydroxide (BTMAOH, TCI, 40% in water) were used as received. Pentamethyl phenyl guanidinium tethered perfluorinated ionomers (M-Nafion-FA-TMG) were prepared by an activated fluorenlyl-amine reaction14 and followed by the methylation with dimethylsulfate. Benzyl trimethyl ammonium (BTMA+) tethered poly(phenylene) ionomers (ATM-PP) were synthesized by an irreversible Diels-Alder reaction. The chemical structures of M-Nafion-FA-TMG and ATM-PP are shown in Figure 1.

Ionomer characterization.— Ionomer dispersion was prepared using a sulfate form of M-Nafion-FA-TMG and a bromide form of ATM-PP. M-Nafion-FA-TMG was dispersed in a mixture of N-methyl pyrrolidone (NMP) and glycerol (1:1 weight ratio) at 120 °C. ATM-PP ionomer was dispersed in a polyhydric alcohol at 120 °C. Brown-colored clear dispersions (solid content 2.5 wt%) were obtained. Hydroxide conductivities of the membranes were determined from AC impedance spectroscopy using a Solartron 1260 gain phase analyzer over a frequency range from 1 Hz to 1 MHz. Weight-based ion exchange capacity (IECW, meq. g−1) was determined by back-titration background currents recorded under N2 atmosphere. The measured voltammograms were corrected for the pre-conditioning step was negligible during the voltammogram scanning started without delay after preconditioning using negative- and positive-going scan (5 mV s−1) between −0.1 and 1.2 V vs. RHE, which guaranteed a consistent initial state of the electrode surface and was essential for obtaining reproducible data. We ran the voltammogram after 10 s delay after preconditioning and obtained very same voltammogram, suggesting that remained oxide was measured using a stylus profilometer (Veeco Dektak 8). The film thicknesses for M-Nafion-FA-TMG and ATM-PP were 5.5 ± 0.5 μm and 3.5 ± 0.5 μm, respectively. The thin films were converted to an auxiliary electrode, and Pt microdisk electrode (100 μm diameter) as a working electrode. Before use, the working electrode was cleaned by repeated procedure of polishing with 0.05 μm alumina slurry (Buehler), rinsing with deionized water (18.2 MΩ, Millipore) and concentrated sulfuric acid until a reproducible cyclic voltammogram was obtained in 0.1 M NaOH. Voltammograms for HOR and ORR in saturated 0.1 M TMG (pH 12.6) and 0.1 M BTMAOH (pH = 12.6) solutions were recorded using a CH Instruments potentiostat model CHI 760D. During the HOR and ORR measurements, the gas feed line was placed slightly above the electrode surface and was essential for obtaining reproducible data. All solution experiments were performed at ambient temperature. The voltammograms were recorded after a 10 s pre-conditioning of the Pt microelectrode at 1.4 V. The voltammogram scanning started without delay after preconditioning using negative- and positive-going scan (5 mV s−1) between −0.1 and 1.2 V vs. RHE, which guaranteed a consistent initial state of the electrode surface and was essential for obtaining reproducible data. We ran the voltammogram after 10 s delay after preconditioning and obtained very same voltammogram, suggesting that remained oxide from the pre-conditioning step was negligible during the voltammogram scanning. The measured voltammograms were corrected for the background currents recorded under N2 atmosphere.

A mini-cell fabricated with a 100 μm diameter Pt disk micro-electrode (Bioanalytical Systems) was used for the electrochemical measurements in the absence of liquid electrolyte (Figure 2). Before the cell was assembled, the microelectrode was cleaned by multiple potential cycling (0.0 ~ 1.4 V vs. RHE) in 0.1 M NaOH. Thin ionomer film was cast onto the electrode tip using 6.0 μL of 2.5 wt% ionomer dispersion and dried in an oven at 80 °C for 24 h. The film thickness was measured using a stylus profilometer (Veeco Dektak 8). The film thicknesses for M-Nafion-FA-TMG and ATM-PP were 5.5 ± 0.5 μm and 3.5 ± 0.5 μm, respectively. The thin films were converted to

### Table I. Physicochemical properties of polymers.

| Property                        | M-Nafion-FA-TMG | ATM-PP |
|---------------------------------|-----------------|--------|
| IECW (meq. g−1)                 | 0.7             | 1.7    |
| Water uptake @ 30 °C Wt. %      | 10              | 83     |
| Vol. %                          | 20              | 97     |
| Hydration number (λ)            | 7.9             | 27.1   |
| IECV(WET) (meq. cm−3)           | 1.1             | 1.0    |
| Hydroxide conductivity (mS cm−1)| 30 °C 10        | 40     |
|                                | 80 °C 20        | 80     |

Figure 1. Chemical structures of (a) phenyl pentamethyl guanidinium functionalized perfluorinated ionomer (M-Nafion-FA-TMG) and (b) benzyl trimethyl ammonium functionalized poly(phenylene) ionomer (ATM-PP).

Figure 2. Schematic diagram of Pt microelectrode mini-cell set-up.
hydroxide form by depositing 6 μl of 0.5 M NaOH solution onto the film. After drying the NaOH solution, the film was subsequently rinsed with deionized water. A Pt foil counter electrode was placed at the side of the microelectrode, and an ATM-PP membrane was used as an anion conduction path between the microelectrode and the Pt foil. The ATM-PP membrane was glued between the Pt microelectrode and the hydrogen reference electrode (6% H2 in Ar[Pt|NaOH (0.1 M)]. An ATM-PP solution in alcohol was used to glue the membrane to both electrodes. After the fabrication, the mini-cell was cured under N2 flow at 40°C for 7 h in order to obtain reproducible data. The HOR and ORR voltammograms were obtained by linear sweep voltammetry using the CHI 760D potentiostat using the same procedure with the solution experiments.

Results and Discussion

Pt/liquid solution interface for HOR.— The HOR voltammograms in 0.1 M TMG and BTMAOH solutions were obtained from the respective anodic voltammetric scans (−0.1 to 1.2 V vs. RHE) after either immersing the electrode in the solution for 30 minutes or preconditioning at 1.4 V for 10 seconds (Figure 3). The HOR activities measured before preconditioning are much inferior compared to those measured after preconditioning in both of 0.1 M TMG and BTMAOH solutions. According to the previous results observed with polycrystalline Pt electrodes in 0.1 M TMAOH,19 the inferior HOR activities obtained before preconditioning are most likely due to the adsorption of the cations on the Pt surface. Since both BTMA+ and TMG+ cations are rather hydrophobic compared to the alkali metal cations,28 they tend to occupy the surface of platinum, where the repulsive interactions with water are reduced. The electronic charge of the cations additionally increased the interaction with negatively charged electrode surface in the potential range. The overall equilibrium is determined by the balance of all attractive and repulsive interactions between the cations, the solvent and the Pt electrode. Upon increase of the electrode potential, i.e., during the preconditioning step, the cations desorb, as the electrostatic interactions between them and the electrode surface become unfavorable, and the electrode surface is exposed. The desorption potential of the cations was determined by comparing two voltammograms measured before and after the preconditioning step: The TMG+ desorbs in the range of 0.2–0.6 V, while the desorption of BTMA+ occurs in the more positive potential range of 0.5–0.75 V. The lower onset desorption potential for TMG+ (~0.2 V) compared to BTMA+ (~0.5 V) is likely owing to the different delocalized electron structure of the cations. After HOR current densities in both electrolytes reach a maximum, the current begins to decrease as a result of the oxide formation on the Pt surface.

It is interesting to note that there is an inflection point at ca., 0.1 V in the voltammograms recorded after preconditioning for the TMG and BTMAOH solutions. This inflection point might suggest the presence of a potential driven reorganization of the adsorbed layers or a structural effect of the cations. In order to establish whether some structural effects of the cations are responsible for the observed inflection points, a HOR voltammogram of Pt was recorded for 0.1 M TMAOH solution after the same preconditioning process. The TMA+ cation has a fixed tetrahedral geometry, which is unlikely to be noticeably altered by the electric field at the interface. The lack of inflection in the voltammogram (Figure 4) suggests that the inflection points in the voltammograms recorded for 0.1 M TMG and BTMAOH solutions may likely be related to the significant charge anisotropy of TMG+ and BTMA+ cations and the high polarizabilities of the phenyl ring and the electron conjugated guanidinium.29 The processes that preceed the main desorption was fast and unaffected by the high potential pretreatment.

The potential dependent cation adsorption/desorption processes are particularly interesting, because unlike typical ionic adsorption they occur slowly. Figure 5 shows HOR voltammograms as a function of the preconditioning potential. As the preconditioning potential increases from 0.2 to 1.4 V, the HOR activities of Pt for both liquid electrolytes improve. The most significant amount of cation desorption in the TMG and TMAOH solutions occurred with the preconditioning.

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Figure 3. HOR polarization plots of Pt microelectrode in (a) 0.1 M TMG and (b) 0.1 M BTMAOH solutions, before and after preconditioning at 1.4 V for 10 seconds. Scan rate: 5 mV s⁻¹.

Figure 4. HOR polarization plots of Pt microelectrode in 0.1 M TMAOH solution after preconditioning at 1.4 V for 10 seconds. Scan rate: 5 mV s⁻¹.
potential of 0.6 V and 1.0 V, respectively. As a result, the HOR activities of Pt in the TMG and BTMAOH solutions became similar after the preconditioning at 1.4 V, reaching ca., 0.37 mA cm$^{-2}$ (TMG) and 0.33 mA cm$^{-2}$ (BTMAOH) at 0.01 V. The lower desorption potential of the TMG$^+$ is also observed as is the case in Figure 3.

In order to investigate the time dependence of the observed phenomena, the HOR voltammograms were measured at 0, 10, and 30 minutes after preconditioning, and followed by repeated preconditioning (Figure 6). The adsorption kinetics in BTMAOH solution is relatively slow compared to that in TMG solution: the process was virtually complete within 10 minutes, whereas it took 30 minutes in BTMAOH solution. After repeated preconditioning at 1.4 V, the HOR activities were fully recovered. This indicates that the adsorption occurs spontaneously and the adsorbates are fully desorbed at 1.4 V, where the Pt surface is covered with its oxide. Similar time-dependent behavior was also observed with much smaller TMA cation. This time-dependent slow adsorption behavior of the organic cations suggests that the cation adsorption is not a typical fast process but is possibly associated with partial charge transfer, significant rearrangements of the layer with coverage and/or anion co-adsorption. It is worth noting that a recent density functional theory study of alkali cation adsorption on metal surfaces concluded that the alkali cation adsorption is accompanied by a partial electron transfer and surface rearrangement of the solvating water molecules.

Pt/ionomer interface for HOR.— Figure 7 shows the HOR voltammograms of the ionomer-coated Pt microelectrodes after preconditioning at 1.4 V for 10 s. The HOR limiting current densities of M-Nafion-FA-TMG- and ATM-PP- coated Pt electrodes were 0.74 mA cm$^{-2}$ disk at 0.28 V and 0.82 mA cm$^{-2}$ disk at 0.87 V, respectively. When the film thickness corrections were applied, the limiting HOR current density for the M-Nafion-FA-TMG-coated electrode was found to be ∼54% higher than that for the ATM-PP-coated electrode. The HOR voltammogram of the M-Nafion-FA-TMG coated Pt electrode bears some similarity and shows similar HOR pattern with that of preconditioned Pt electrode in the 0.1 M TMG solution (Figure 7a). The HOR polarization of the ATM-PP ionomer coated Pt microelectrode, on the other hand, bears some similarity with the HOR voltammogram measured before preconditioning in the 0.1 M BTMAOH solution, as demonstrated by the presence of a peak in the far anodic portion of the voltammogram. The apparent cation desorption potential of the ATM-PP ionomer (Figure 7b) is ∼0.6 V, i.e., it is slightly more positive than the respective potential measured for the BTMAOH solution. The similarity of HOR voltammograms measured for the ATM-PP-coated electrode after preconditioning with that of BTMAOH electrolyte before preconditioning suggests that the tethered BTMA groups likely occupy the immediate vicinity of the electrode surface most likely due to the polymer chain rigidity and steric hindrances. Upon applying low potential, the quaternary

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**Figure 5.** Effects of preconditioning potential on desorption of (a) TMG$^+$ and (b) BTMA$^+$ from the Pt microelectrode. The HOR polarization plots were obtained after preconditioning at each specified potential for 10 s after immersing the Pt microelectrode in the 0.1 M TMG and in the 0.1 M BTMAOH electrolytes for 30 min. Scan rate: 5 mV s$^{-1}$.

**Figure 6.** Time-dependent adsorption of (a) TMG$^+$ and (b) BTMA$^+$ on Pt microelectrode. The HOR polarization plots were obtained without preconditioning after immersing the Pt microelectrode in 0.1 M TMG and BTMAOH electrolytes for each specified time. Scan rate: 5 mV s$^{-1}$.
ammonium ions in BTMAOH solutions are able to quickly re-adsorb on the electrode surface. This behavior strongly contrasts that observed for M-Nafion-FA-TMG, which provides sufficient mobility of the interfacial cationic groups to allow them to move away from the Pt surface like the TMG$^+$ cations during the preconditioning step. Similar ion mobility derived from segmental motion of polymers for acid systems was suggested by Eisenberg, and observed in alkyl ammonium, sulfonated polystyrene, and Nafions.

**Long term HOR behavior.**— Long term HOR behaviors at Pt/ionomer interfaces were investigated. In the experiments, the mini-cell was exposed to water saturated N$_2$ at 40°C for 50 h without applying a potential. The chemical degradation of polymer electrolytes under such experimental conditions is likely negligible based on our previous results. Figure 8a and 8b show the HOR voltammograms recorded for M-Nafion-FA-TMG-and ATM-PP-coated Pt microelectrodes after 30 and 50 hour exposure to the humidified nitrogen. The HOR voltammogram recorded for the M-Nafion-FA-TMG coated Pt electrode differs only slightly from the initial voltammogram; the HOR current density at 0.01 V changed from 0.11 to 0.099 mA cm$^{-2}$disk. The HOR voltammetry measured for the ATM-PP coated Pt electrode exhibited more significant changes; the HOR current density at 0.01 V was continuously changing from 0.11 to 0.064 mA cm$^{-2}$disk over the 50 hour period. This finding indicates that the process to reach an equilibrium structure for the layer of adsorbed BTMAOH$^+$ cationic groups is inherently slow.

**Pt/liquid solution interface for ORR.**— The ORR voltammograms of Pt microelectrode in 0.1 M TMG and BTMAOH electrolytes were measured between 0 and 1.2 V after preconditioning at 1.4 V for 10 seconds (Figure 9). While the onset potentials for two electrolytes were similar, ca., $\sim$1.08 V, the half-wave potential, E$_{1/2}$, in 0.1 M TMG was significantly lower than that in 0.1 M BTMAOH, i.e., 0.66 V vs. 0.86 V. This indicates that the ORR in 0.1 M TMG solution is significantly inhibited as the potential decreases. The activity difference should be related to the nature of the cation. According to Markovic et al. cations with higher hydration energy such as Li$^+$ interact more strongly with OH species (OHad) on Pt surface than the less hydrated cations such as Cs$^+$. The strong hydration of cation leads to a higher concentration of cation-(H$_2$O)$_x$OHad clusters near the Pt surface, resulting in slower ORR kinetics. Although this is a plausible explanation for the alkali metal cation effects on ORR of Pt, it cannot explain the inferior ORR performance of Pt in the TMG solution compared in the BTMAOH solution. The hydration energy of guanidinium cations has been known to be one of the weakest ones among organic cations and thus better ORR kinetics could have been expected. This unexpectedly lower ORR activity of Pt in the TMG solution is perhaps related to the structural effect of guanidinium.
Potential range is similar to the onset potential of BTMA potential-dependent adsorption of the BTMA current reduction in the BTMAOH solution seem to be related to the high cathodic overpotentials corresponding formally to the limiting face and block the Pt reaction sites during ORR. Further verification H2O2 formation.

unblocking of the electrode surface and also reducing the extent of desorption may lead to a current increase due to two effects, namely and weakly hydrated TMG with each other. The AIMD simulation suggests that the hydrophobic and ordinary cations, such as ammonium, do not form contact ion pairs (planarity and a delocalized inhomogeneous electronic distribution).

The formation of same-charge contact ion pairs requires specific geometric and electronic structure properties (planarity and a delocalized inhomogeneous electronic distribution). Ordinary cations, such as ammonium, do not form contact ion pairs with each other. The AIMD simulation suggests that the hydrophobic and weakly hydrated TMG+ can either directly adsorb onto the Pt surface or form a TMG2+-TMG+ in the proximity of the electrode surface and block the Pt reaction sites during ORR. Further verification for this hypothesis may be needed. The ORR current fluctuations at high cathodic overpotentials corresponding formally to the limiting current reduction in the BTMAOH solution seem to be related to the potential-dependent adsorption of the BTMA+ cation. The respective potential range is similar to the onset potential of BTMA+ desorption during HOR anodic scan. In TMG solution, a steady increase of the current was observed as potential increased from 0.05 to 0.3 V most likely due to the desorption of TMG+ from Pt surface. The desorption may lead to a current increase due to two effects, namely unblocking of the electrode surface and also reducing the extent of H2O2 formation.

Ab initio molecular dynamics (AIMD) simulations of a pair of guanidinium cations in liquid water indicated that guanidinium cations can directly pair with each other due to their planarity and delocalized electronic distribution. The formation of same-charge contact ion pairs requires specific geometric and electronic structure properties (planarity and a delocalized inhomogeneous electronic distribution). Ordinary cations, such as ammonium, do not form contact ion pairs with each other. The AIMD simulation suggests that the hydrophobic and weakly hydrated TMG+ can either directly adsorb onto the Pt surface or form a TMG2+-TMG+ in the proximity of the electrode surface and block the Pt reaction sites during ORR. Further verification for this hypothesis may be needed. The ORR current fluctuations at high cathodic overpotentials corresponding formally to the limiting current reduction in the BTMAOH solution seem to be related to the potential-dependent adsorption of the BTMA+ cation. The respective potential range is similar to the onset potential of BTMA+ desorption during HOR anodic scan. In TMG solution, a steady increase of the current was observed as potential increased from 0.05 to 0.3 V most likely due to the desorption of TMG+ from Pt surface. The desorption may lead to a current increase due to two effects, namely unblocking of the electrode surface and also reducing the extent of H2O2 formation.

Figure 9. ORR voltammograms for Pt microelectrode in 0.1 M TMG and BTMAOH electrolytes; positive-going sweep from 0 to 1.2 V after preconditioning at 1.4 V for 10 s. Scan rate: 5 mV s−1.

Figure 10. ORR voltammograms recorded using M-Nafion-FA-TMG- and ATM-PP-coated Pt microelectrodes as a function of time. In the long term experiments, the mini cell was exposed to water saturated N2 at 40 °C for 50 h without applying potential. The onset potential for the M-Nafion-FA-TMG-coated Pt electrode increased from 0.97 to 0.99 V after 50 h, while the onset potential for the ATM-PP coated Pt electrode slightly decreased from 0.97 to 0.96 V. In addition, a prominent peak at ~0.6 V for the ATM-PP-coated Pt electrode, probably related to the changes in cation adsorption over time, appeared in the voltammogram. This is consistent with long term HOR behaviors that also showed cationic group adsorption for the ATM-PP-coated Pt electrode. The half-wave potential of the M-Nafion-FA-TMG coated electrode gradually increased from 0.77 V (7 h) to 0.78 V (30 h) and to 0.80 V (50 h), while the half-wave potential of the ATM-PP-coated electrode slightly decreased from 0.80 V (7 h) to 0.79 V (30 and 50 h). The limiting current measured for both electrodes increased. For the M-Nafion-FA-TMG coated electrode, the limiting current increased from −1.36 (7 h) to −1.51 (30 h) to −1.58 mAm−2 disk (50 h). For the ATM-PP coated electrode, the limiting current increased from −0.89 (7 h) to −0.94 (30 h) to −1.00 mAm−2 disk (50 h). The limiting current changes were not caused by film thickness changes as indicated by our other experiments involving 300 h life tests under the same experimental conditions, but rather by increases in the respective oxygen permeability. From the increased limiting currents,
Figure 11. ORR voltammograms recorded for polymer coated Pt microelectrodes as a function of equilibration time under saturated N2, 40°C and 100% RH. (a) M-Nafion-FA-TMG and (b) ATM-PP; Preconditioning: 1.4 V for 10 s. Scan rate: 5 mV s⁻¹.

Figure 12. ORR polarization curves of Pt microelectrode coated with Nafion as a function of time under O2 at 40°C, 30% RH. The film thickness is 8.7 μm, and the ORR curves were obtained after preconditioning at 1.4 V for 10 s with 5 mV s⁻¹ of scanning rate. For the longer term ORR behaviors, the Nafion coated Pt microelectrode was equilibrated under N2 at 40°C, 30% RH without applying potential.

Conclusions

We investigated the HOR and ORR behaviors of Pt at the Pt/alkaline ionomer interface using two structurally different alkaline polymer electrolytes. This research resulted in the following conclusions:

1. The HOR activities of Pt in 0.1 M TMG and BTMAOH solutions measured before preconditioning at 1.4 V are much inferior compared to those measured after preconditioning, probably due to the organic cation adsorption. The HOR activity was recovered at 0.2 and 0.5 V for TMG and BTMAOH solutions, respectively, where possible desorption of the cations occurred.

2. The HOR voltammogram of the M-Nafion-FA-TMG coated-Pt electrode after preconditioning at 1.4 V showed similar HOR pattern with that of preconditioned Pt electrode in the 0.1 M TMG solution. In contrast, the HOR polarization of the ATM-PP ionomer coated Pt microelectrode remained poor after preconditioning at 1.4 V, probably because of the less cation mobility driven by the chain stiffness of ATM-PP.

3. More positive half-wave potential for ORR at Pt/M-Nafion-FA-TMG compared to that at Pt/TMG solution emphasizes the benefit of using polymer electrolytes over using liquid electrolyte in alkaline fuel cells.

4. The ORR activity of the M-Nafion-FA-TMG-coated Pt electrode is comparable to that of the ATM-PP-coated Pt electrode. M-Nafion-FA-TMG has 2.5 times higher O2 permeability than the aromatic ATM-PP.

5. The onset and half-wave potentials and O2 limiting current for the polymer coated Pt microelectrodes notably changed as the equilibration time increased. This phenomenon is likely responsible for the known relaxation behavior of polymer electrolyte fuel cells under operating conditions.

Acknowledgment

Los Alamos National Laboratory is operated for the US Department of Energy by Los Alamos National Security LLC under Contract DE-AC52-06NA25396. We thank US DOE Fuel Cell Technologies Program, Technology Development Manager Dr. Nancy Garland, for financial support. S.D.Y. acknowledges financial support from Korea Institute of Energy Research, South Korea (BS-2415-01), and from the International Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, South Korea (20138520030780).
