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Pt-Free Cathode Catalyst Performance in H_2/O_2 Anion-Exchange Membrane Fuel Cells (AMFCs)

A. Filpi[a,b], M. Boccia[a], H. A. Gasteiger[a]

[a] Acta S.p.A., via di Lavoria 56/G, I-56040 Crespina (PI), Italy
[b] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

H_2/O_2 AMFCs enable the use of Platinum Group Metal (PGM) free Membrane Electrode Assemblies (MEAs), especially for the Oxygen Reduction Reaction (ORR). A promising catalysts for the ORR (Acta's "K14"), has been developed and tested using Rotating Disk Electrode (RDE) analysis, showing promising performance. In this paper we characterize current Anion-Exchange Membranes (AMs), show the fuel cell activity of AM-based MEAs prepared with K14 ORR catalyst, and compare their performance with the kinetic and ohmic limits projected from the membrane and catalyst properties. The data and projections show promising results for this technology.

Introduction

Due to reasons of excessive cost and supply limitations of platinum, large-scale application of H_2/O_2 Polymer Electrolyte Membrane Fuel Cells (PEMFCs) would require strongly reduced Pt loadings. To meet this requirement, the Pt specific power density would have to be reduced to <0.2 g_{Pt}/kW at cell voltages of ≥0.6 V (to maintain high fuel cell energy conversion efficiencies of > 55%). State-of-the-art Pt loading are ≈0.4 to 0.5 mg_{Pt}/cm^2_{MEA}, corresponding to Pt-specific power densities of ≈0.5 g_{Pt}/kW. Therefore, to reach the above targets, Pt loadings of ≤0.15 mg_{Pt}/cm^2_{MEA} are needed, which would require improved cathode catalysts with an approximately four-fold higher activity compared to Pt/C (1).

Anion-exchange membrane fuel cells (AMFCs), on the other hand, promise to enable the use of PGM-free catalysts. In the last 5 years, novel anion-exchange polymers (membranes and solubilized ionomers) have been developed, opening a new challenge to develop ionomer-bonded AM-based MEAs analogous to PEMFCs, and recent literature results are promising (2, 3).

In the present work, a benchmark AM and Acta's PGM-free ORR catalyst "K14" were used and evaluated, showing promising properties for AMFC applications. In order to estimate the potential of this technology, theoretical performance projections are made, using the measured properties of a current AM and Acta's K14 catalyst. Kinetic activity data for K14 catalyst were collected using RDE analysis (4). Catalyst Coated Membranes (CCMs) using current benchmark AMs and solubilized anion-exchange ionomers were prepared with either conventional Pt/C or non-PGM K14 catalyst, evaluated in a H_2/O_2 AMFC, and compared to projected theoretical data.

Experimental

AM Materials Characterization

Deionized liquid water (ρ≥10MΩ·cm) was used in all experiments. A multi-channel potentiostat/galvanostat, having an impedance channel and a 4A current booster (VMP3 from Bio-Logic SA) was used to perform electrochemical impedance spectroscopy measurements.

Ion-Exchange Capacity (IEC). The IEC of AM materials was determinated by acid-base back-titration: an AM piece was pretreated in 1M KOH at 50°C for 1h to exchange to the OH-form, the piece was then washed under exclusion of air using N_2-degased water and soaked for 30 min in a exact amount of a standardized HCl solution, where OH^- (the counteranion of the ion-exchange groups, IEGs) is neutralized. Excess of HCl was backtitrated with standardized KOH using visual or potentiometric end-point detection.

Water Uptake (WU). A tailed flask containing continuously N_2-degased water was used. The temperature control was ensured using a thermostatic oil bath and the weight of an AM piece (either a membrane or the ionomer cast as membrane) was determined by a four-digits analytical balance. Dry weight of the AM piece was measured after 24h equilibration at 60°C in an oven. The AM was pretreated in 1M KOH (or 1M KCl) at 50°C for 1h in order to exchange it into the OH-form (Cl-form). Wet weight values were measured after 30 min equilibration in the tailed flask at the envisaged temperature. The water uptake, as mass percentage, was calculated using equation [1]:

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \cdot 100 \qquad [1]$$

where W_{wet} and W_{dry} are the wet and dry AM piece weight, respectively, averaged over 3 measurements, at each temperature.

In-plane (IP) conductivity. IP conductivity was measured using a Bekktech PTFE 4-probe flow-cell, assembled with a 5 cm^2 cell hardware supplied by Fuel Cell Tecnologies, allowing in-situ AM exchange to the OH-form (Cl-form) flowing a 1M KOH (or 1M KCl) solution. This was followed by removal of the excess electrolyte via a continuous flow of N_2-degased water, such that the AM cannot get contaminated by bicarbonate ions which are present in air-exposed deionized water. Fig. 1 (a) shows a typical Nyquist plot obtained for such measurements: the high-frequency arc represents a parallel RC circuit coming from membrane bulk resistance and capacitance, while the low-frequency arc is an artifact coming from Pt-wire/AM interfacial impedance (5). Membrane resistance was calculated by fitting the impedance data to an RC circuit between 100 kHz and 10 kHz (i.e. before the low-frequency arc) to prevent artifacts.

Through-plane (TP) conductivity. The TP conductivity was measured using a 5 cm^2 cell hardware supplied by Fuel Cell Tecnology allowing in-situ ion exchange, analogous to the in-plane tests, again carefully avoiding air exposure of the AM materials. Pt based anion-exchange ionomer based CCMs, prepared as described below, were used. Fig. 1 (b) shows a typical Nyquist Plot obtained for such measurements: at high frequency, a

transmission line shows up (i.e., a 45° line), coming from the ionic resistance of the electrode, while at low frequencies the graph approaches a vertical line, due to the electrode capacitance. The contact resistance was measured using a cell assembled without the membrane ($R_{contact} \approx 5m\Omega$). Membrane resistance was calculated extrapolating the 45° line to the real axes and subtracting the measured contact resistance.

Water Uptake, Ionic Exchange Capacity, in-plane and through-plane conductivity were also measured for Nafion® 115, serving as benchmark for cation-exchange materials, and using 0.5M H_2SO_4 in place of KOH to exchange to the H-form; Nafion® ionomer bonded Pt/C electrodes were used in this case for through-plane conductivity measurements.

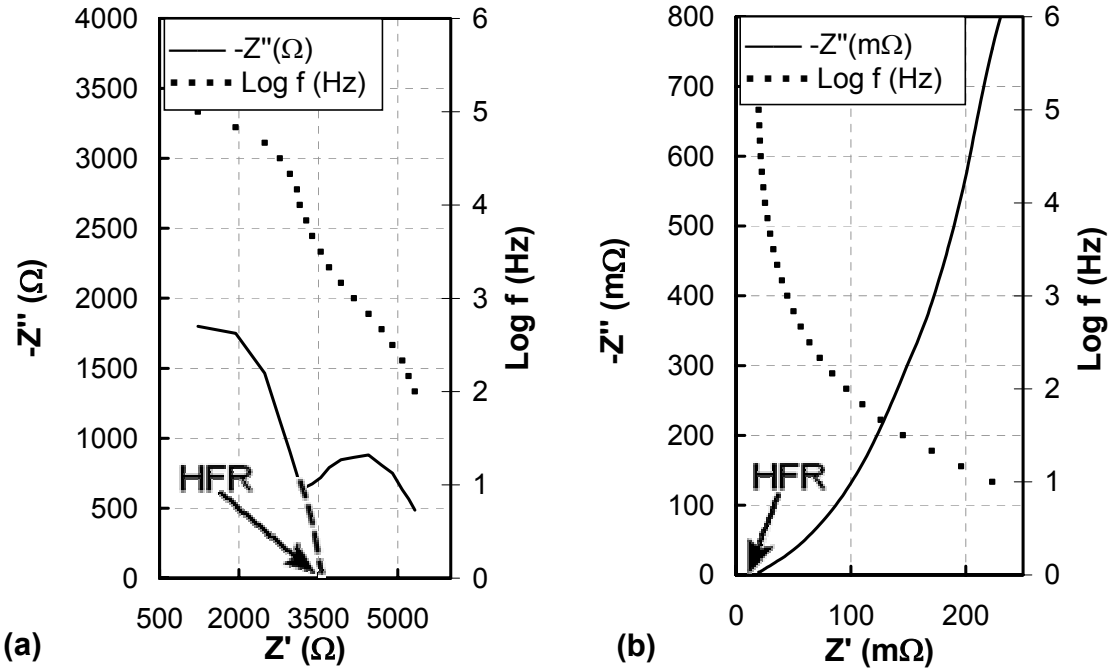

Figure 1. (a) 4-probe impedance spectra for an in-plane conductivity measurement, in flowing N_2-degased deionized liquid water ($\rho \geq 10M\Omega \cdot cm$), of a cast AM piece having width of 1.15 cm and wet thickness of 120 μm. Frequency range 100 kHz – 100 Hz, voltage amplitude 10 mV. **(b)** Impedance spectra for a through-plane conductivity measurement in flowing N_2-degased deionized liquid water ($\rho \geq 10M\Omega \cdot cm$), of a cast AM of 5 cm^2 area and a wet thickness 40 μm. Anion-exchange ionomer bonded Pt/C electrodes were used, having a loading of 0.66 mg_{Pt}/cm^2_{MEA}, using SGL carbon paper (25BC) with a microporous layer as diffusion medium. Frequency range 100 kHz – 10 Hz, voltage amplitude 5 mV.

MEA Preparation

For AMFC testing and anion-exchange measurements, a benchmark membrane and ionomer solubilized in alcohol were used, whereas Nafion® 115 membrane (Fuel Cell Scientific) and a solution of Nafion® in a mixture of lower aliphatic alcohols and water (Aldrich) were used for cation-exchange measurements. CCMs were prepared either using a 40 wt% Pt on Vulcan catalyst (BASF) or a transition metal based catalyst supported on carbon (K14 from Acta) (4). The catalyst was mixed with a certain amount of water, alcohol, and ionomer solution, and then sonicated to obtain a homogeneus ink.

The obtained ink was coated on a decal and transferred to the membrane by hotpressing to obtain CCMs. SGL carbon paper (25BC) with a microporous layer was used as diffusion medium.

H_2/O_2 AMFC Tests.

Cells were assembled using 5 cm^2 stainless steel single cell hardware from Fuel Cell Technologies and MEAs prepared as described above. Pt/C based electrodes were used on the anode side, whereas Pt/C or K14 based electrodes were used on the cathode side. PTFE gasket thickness was selected to obtained an overall strain of ≈25% to guarantee good electrical contact and sealing. H_2 and O_2 (purity of N5.0) were provided by Sol. Gas flows, humidification, temperature and cell temperature were controlled using a Scribner 850C test station. MEAs were conditioned by cycling between OCV and 200 mV cell potential for 15 minutes/step (Arbin BT-2000), till stable performance between two cycles was observed. Polarization curves were collected applying 3 minutes long constant voltage steps in 50 mV intervals, recording the last 30 seconds, from OCV to 200 mV.

Results

AM Materials Characterization

Ion Exchange Capacity (IEC). IEC values, measured for the AM benchmark and Nafion® 115 are 1.84 and 0.87 meq/g, respectively. Since the density of the AM (≈1,1 g/cm^3) is nearly half compared to Nafion® 115 (≈2 g/cm^3), the volumetric IEC is nearly the same for the two materials: ≈ 2 meq/cm^3 for the AM benchmark and ≈1,8 meq/cm^3 for Nafion® 115, which would suggest that similar conductivities could be obtained.

Water Uptake (WU). Fig. 2 shows WU as mass percentage (wt%) in liquid water, calculated using equation [1]. While the benchmark AM, in the OH-form, has a higher wt% WU compared to Nafion® 115, its volumetric swelling is essentially the same due to its nearly two-fold lower density compared to 1100EW Nafion®. Therefore, from the point of view of water uptake, the current AM benchmark is expected to be very suitable to applications in fuel cells and electrolyzers, where low volumetric swelling is required for mechanical stability. Moreover, WU variations with temperature of the AM benchmark in the OH-form are rather small, such that the thickness of a pre-swollen membrane will not change significantly during conductivity measurements as a function of temperature (for this reason, all conductivity measurements are referenced to the thickness of a pre-swollen membrane). Contrary to the benchmark anion-exchange membrane, the solubilized benchmark ionomer has a very high WU; while this is a clear disadvantage for electrode design, it still was acceptable for the proof-of-concept AMFC tests shown later.

Since most AM materials are prepared and supplied in their chloride-form, we also examined the WU in this ionic form. The chloride-form of the AM benchmark exhibits significantly lower WU (see Fig. 2), probably due to the different polarizability and

ionic-radii of chloride and hydroxyl ions. Since the differences between the OH-form and the Cl-form are quite significant, the evaluation of anion-exchange membranes and ionomers should always be done in the OH-form, expecially if inferences are to be drawn with regards to the suitability of a new AM material for AMFC and AME applications, which require the OH-form.

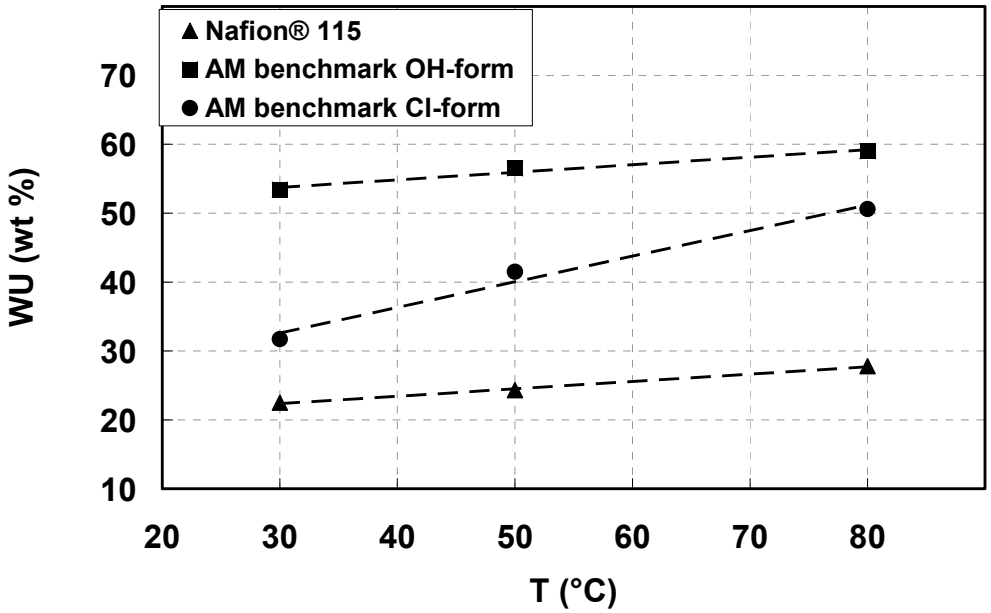

Figure 2. Water uptake as mass percentage of AM benchmark and Nafion® 115, measured in liquid water at different temperatures. The mean error over a set of 5 measurements at each temperature is ≈3 units of wt % for the AM benchmark values (both OH-form and Cl-form), and ≈1 unit of wt % for Nafion® 115.

A more fundamental parameter to characterize the WU is the so-called λ-value, expressing the mean number of water molecules per ion-exchange group. Being independent of the IEC and density of the material, it allows for a better comparison between different materials. The WU expressed as λ was calculated using equation [2]:

$$\lambda = \frac{WU(\%) \cdot 10}{IEC \cdot MW_{water}} \qquad [2]$$

where WU(%) is expressed as mass percentage, IEC is expressed as meq/$g_{polymer}$, and MW_{water} is water molecular weight. In terms of λ, WU values for the AM benchmark in the OH-form are close to Nafion® 115, as shown in Fig. 3. In general, λ-values should remain below 30 in the operating temperature range in order to ensure long-term stability of the material.

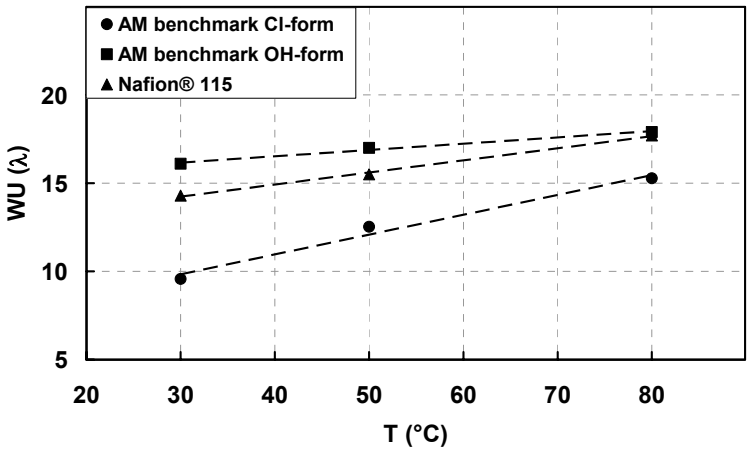

Figure 3. Water uptake in terms of λ (i.e. water molecules per ionic-exchange group) of AM benchmark and Nafion® 115, measured in liquid water at different temperatures. The mean error, over a set of 5 measurements at each temperature is ≈0,9 units of wt % for the AM benchmark values (both OH-form and Cl-form), and ≈0,3 units of wt % for Nafion® 115.

Conductivity. Fig. 4 shows the in-plane (full lines) and through-plane (dashed lines) conductivities of the AM benchmark and Nafion® 115. Both materials exhibit isotropic behaviour, having the same conductivities for in-plane and through-plane. Whilst the conductivities for the AM benchmark in the OH-form is only half compared to Nafion® 115, this result is very encouraging since these values are already high enough to develop AMFC and AM-electrolyzers with sufficiently low ohmic losses at high current densities. For example, a conductivity of ≈0.07 S/cm at 80°C for the 40 μm thick AM benchmark (Fig. 4) would correspond to ohmic losses of only ≈60 mV at 1 A/cm^2. In addition, considering that the conductance at infinite dilution of OH^- in water is nearly half compared to H_3O^+, and that the two materials have the same volumetric IEC, the conductivity of the AM benchmark is quite excellent. Also, the conductivity of the AM benchmark in the OH-form compares favorably with the literature, which reports OH^- conductivities of ≈30 mS/cm at 50°C in H_2O_{liquid} (6) vs. the ≈50 mS/cm shown in Fig. 4.

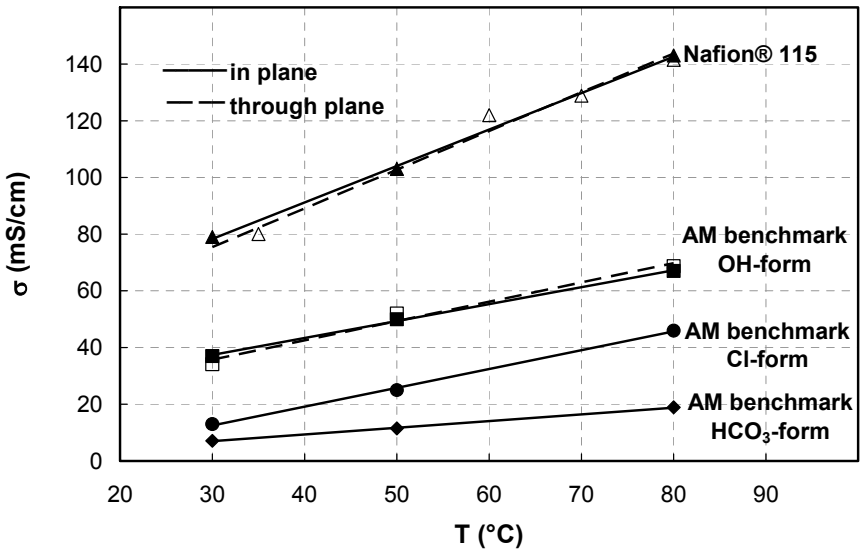

Figure 4. In-plane (full-lines and filled symbols) and through-plane (dashed-lines and empty symbols) conductivities of AM benchmark and Nafion® 115 in liquid water vs. temperatures. The mean error, over a set of 3 measurements at each temperature is ≈2 mS/cm for in-plane values, and ≈3 mS/cm for through-plane values. Conductivity data are referenced to thickness of the pre-swollen membranes (see text).

Consistent with the lower conductance at infinite dilution for Cl^- in water (approximately one half of that of OH^-), the conductivity of the Cl-form of the AM benchmark is ≈2-fold lower than that of the OH-form. Since bicarbonate ions contamination can occur, as discussed in the experimental part, conductivity for the HCO_3-form of AM benchmark was also measured. It is ≈4-fold lower than that of the OH-form, again consistent with the approximately 4-fold lower equivalent ionic conductance of bicarbonate compared to hydroxide (see Fig. 4). To figure out the influence of CO_2 contained in the air on ionic conductivity, a piece of the AM benchmark has been converted to the OH-form and equilibrated in deionized water exposed to air for 1 day. The conductivity of the air exposed-form, reported in Table I, is exactly the same as the in-situ exchanged HCO_3-form. This suggests that bicarbonate formed by the absorption of CO_2 from air can replace the hydroxide ions from the membrane. Therefore, it is clear that measurements of anion exchange membrane properties are affected by air exposure, which must be avoided in experimental procedures, as was done in our experiments in a flow cell using carefully N_2-degased water. This may also explain why essentially identical conductivities are reported for the hydroxide and carbonate form of anion exchange membranes in the literature (3).

Table I. Effect of CO_2 contained in air on the IP conductivity in liquid water of the AM benchmark at 30°C.

air exposed-form	HCO_3-form	OH-form
7 mS/cm	7 mS/cm	37 mS/cm

Fig. 5 shows the Arrhenius plot of the conductivity of the AM benchmark in the OH-form and Nafion® 115 in the proton form. Both of them show a linear behaviour with temperature, yielding activation energies of ≈11 kJ/mol, suggesting a similar transport mechanism.

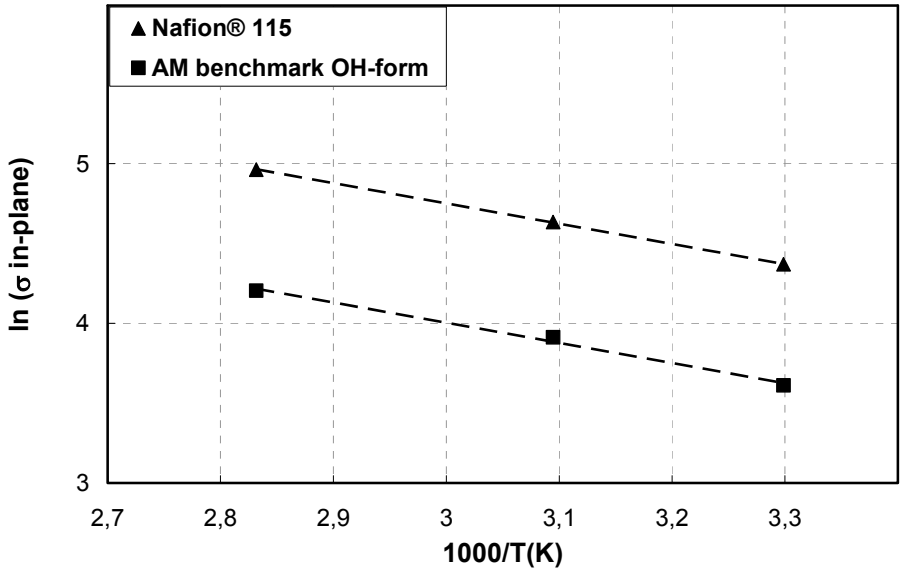

Figure 5. Arrhenius plot for in-plane conductivity in liquid water for AM benchmark and Nafion® 115 (base on the data shown in Fig. 4).

Overall, the balance between conductivity and water uptake of the AM benchmark is quite excellent and compares very well to Nafion® 115. At the same time, while the

conductivity of the solubilized anion-exchange ionomer is essentially identical with that of the AM benchmark (shown in Fig. 4), its water uptake is several times higher. However, improved solubilized ionomers are emerging, which show water uptake and conductivity values essentially identical to the anion-exchange membrane benchmark, so that significantly improved electrodes should be available within short time.

H_2/O_2 AMFC Performance

Pt/Pt CCMs. Fig. 6 shows the measured performance (squares) of a H_2/O_2 AMFC at 80°C using a Pt/C-based CCM prepared as described before. At 0.6V the measured power density is ≈140mW/cm^2. While this is ≈10 times smaller than what one would get with Nafion® 111 based PEMFCs under similar conditions (7), this result is very promising considering the early stage of this technology, and also compares very well with other literature data for AMFCs (2,6). The triangles in Fig. 1, on the other hand, is the estimated AMFC performance for perfectly designed MEAs, based on the known kinetic and ohmic losses (see below). The difference between the actual and the projected performance is indicated as "transport losses", which are currently undefined losses. They could arise from gas transport resistances, ionic transport resistances in the electrode and pH gradients originating from foreign anions (8).

The estimated kinetic and ohmic limit discussed above is obtained by considering that the cell potential, E_{cell}, can defined by the following equation:

$$E_{cell} = E_{cathode} - E_{anode} - i \cdot R_{\Omega} - \eta_{tx} \quad [3]$$

where $E_{cathode}$ is the O_2 cathode potential, E_{anode} is the H_2 anode potential, assumed to be ≈0 (having pure hydrogen and a Pt/C electrode), i is the current density, R_{Ω} is the ohmic resistance (arising from contact and membrane resistances), and η_{tx} is the transport overpotential, which is considered to be zero for the "ideal" electrode. The ohmic resistance was calculated using the following equation:

$$R_{\Omega} = \frac{t_{wet}}{\sigma_{membrane}} + R_{contact} \quad [4]$$

where t_{wet} is the wet thickness of the membrane (≈40 μm), $\sigma_{membrane}$ is the membrane conductivity (≈70 mS/cm from Fig. 4), and $R_{contact}$ is the electric contact resistance between current collector and gas diffusion layer (≈0.025 Ω·cm^2). The cathode potential was calculated, assuming simple Tafel kinetics, i.e. only one Tafel slope, using the following equation:

$$E_{cathode} = 0.9V - TS \cdot \log(i/i_{0.9V}) \quad [5]$$

where TS is the Tafel Slope and $i_{0.9V}$ is the current density at 0.9V vs. RHE (reversible hydrogen electrode potential) at the operating conditions (80°C, 50kPa O_2 partial pressure). To estimate $i_{0.9V}$ at the cell conditions, rotating disk electrode data at 25°C and 100kPa O_2 were used (4). The catalyst mass activity is estimated to be about the same at AMFC test conditions (i.e., ≈0.03A/mg$_{Pt}$ at 0.9V vs. RHE with a Tafel slope of ≈100mV/dec.), assuming that the ORR activity is first order with respect to the O_2 partial pressure (i.e. 0.5x activity from 100kPa p_{O2} RDE conditions to 50kPa p_{O2} in the AMFC)

and that the activation energy at 0.9V is similar to what was measured in PEMFCs for Pt/C, namely ≈10 kJ/mol (i.e., 2x activity from 25°C RDE to 80°C AMFC) (9). Combining equations 3, 4, and 5, we obtain the expression for the kinetically and ohmically limited cell potential based on the catalyst and membrane properties:

$$E_{kin+\Omega} = 0.9V - TS \cdot \log\left(i/i_{0.9V}\right) - i \cdot \left(R_{contact} + \frac{t_{wet}}{\sigma_{membrane}} \right) \qquad [6]$$

As discussed above, the estimated kinetically and ohmically limited performance is shown by the triangular symbols in Fig. 7. As can be seen, the actual (squares in Fig. 7) and the projected (triangles in Fig. 7) performance coincide at low current density, demonstrating that the ionomer does not poison the ORR kinetics. At higher current densities, transport losses make the experimental curve deviate from the projected limit.

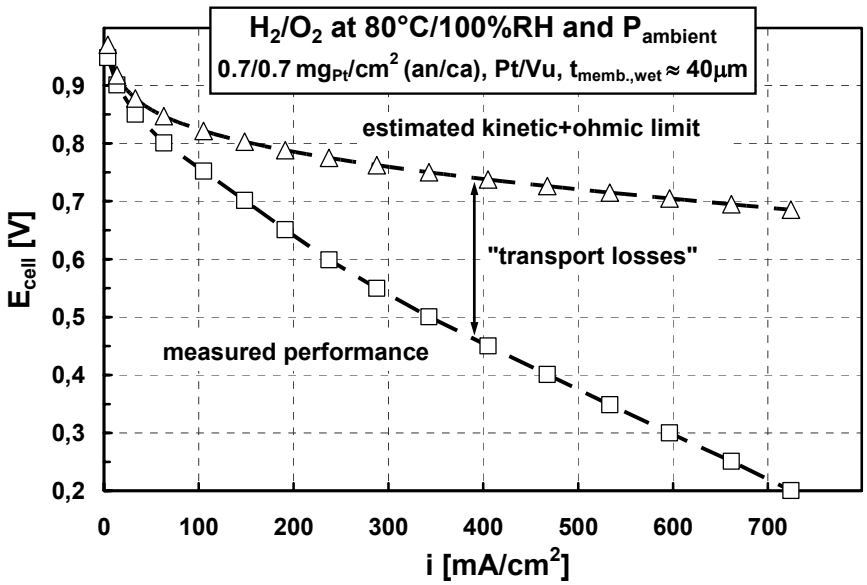

Figure 6. AMFC performance with fully humidified H_2/O_2 (70/140 sccm flows) at ambient pressure and 80°C. Ionomer-bonded 5 cm^2 CCMs were based on a commercial benchmark membrane (t_{wet} ≈40 µm) with catalyst loadings of 0.7/0.7 mg_{Pt}/cm^2 (anode/cathode), using a 40%wt. Pt/Vulcan catalyst. Data were obtained after 3 minutes hold at each potential. Square symbols denote the measured performance, while triangles represent the approximate kinetic and ohmic limit.

Pt/K14 CCMs. In Fig. 7, the same analysis has been applied to an AM-CCM using a non-PGM ORR catalyst (ACTA's K14) and tested in a H_2/O_2 AMFC. Compared to Fig. 6, the power density at 0.6V is not so different (110 vs. 140 mW/cm^2), which to our knowledge is the highest performance ever reported for an AMFC using a non-PGM cathode catalyst, clearly demonstrating the high potential of the AMFC technology to reduce the PGM content by a large factor, or even to eliminate it. However, a limiting current appears at ≈0.2A/cm^2, which is probably due to non-optimized MEA design. At the same time the theoretical curve based on the RDE kinetics of K14 (triangles) does not match with the experimental data (squares) at low current density (4). This behavior could be due to significant kinetic dependence of the non-PGM ORR catalyst on pH, contrary to a Pt catalyst (10). Further tests are being conducted to investigate this difference and to optimize the structure of the electrodes.

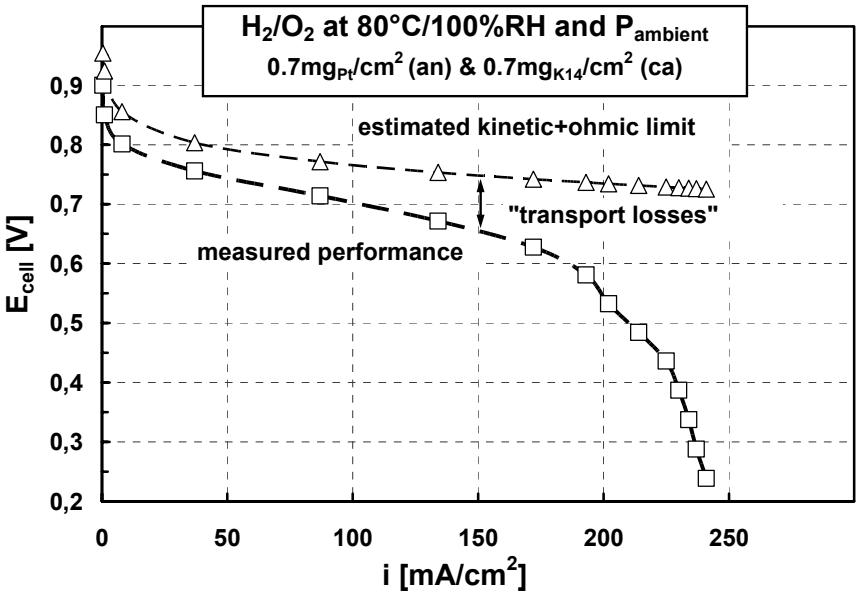

Figure 7: AMFC performance with fully humidified H_2/O_2 (70/140 sccm flows) at ambient pressure and 80°C. Ionomer-bonded 5 cm^2 CCMs were based on a commercial benchmark membrane (t_{wet} ≈40 μm) with anode loadings of 0.7 mg_{Pt}/cm^2 (40%wt. Pt/Vulcan) and cathode loadings of 0.7 $mg_{catalyst}/cm^2$ using Acta's non-PGM cathode catalyst. Data were obtained after 3 minutes hold at each potential. Square symbols denote the measured performance, while triangles represent the approximate kinetic and ohmic limit.

Conclusions

To develop H_2/O_2 AMFCs, viable anion-exchange membranes are already available. At the same time, while the conductivity of currently available solubilized ionomers is also quite excellent, the water uptake is still too high, but improved materials are recently emerging, promising improved MEA performance and durability. Being early in the technology development of AMFCs, the results obtained for a Pt/Pt based CCMs in H_2/O_2 AMFCs are promising, and work is in progress in our laboratory to advance MEA design, and incorporate improved materials (both catalysts and ionomers).

Results were also presented showing AMFCs based on a non-PGM cathode catalyst (Acta's K14). At 0.6 V these non-PGM cathode catalyst based CCMs, are comparable in activity to Pt-based CCMs. While still a lot of work has yet to be done regarding MEA optimization, these results are very encouraging and suggest that non-PGM polymer membrane based fuel cell development may have a bright future.

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