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Measurement and adjustment of proton activity in solid polymer electrolytes

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Abstract

Technological progress in electrochemical energy conversion devices requires new solid polymer electrolyte membrane (PEM) materials with particular properties. The strongly acidic nature of Nafion® is not always desirable; for instance, CO2 electroreduction requires a low proton activity to avoid excess hydrogen evolution. This communication presents a novel measurement technique for determining the acidity of a PEM, using a pH-sensitive electrode half-cell attached to the membrane sample, connected to a reference electrode via a salt bridge. A dynamic hydrogen electrode on platinised-platinum surface (DHE) was found to give repeatable results within 5% uncertainty. Several membranes based on Nafion® impregnated with various basic species were tested, as well as an anion-exchange membrane and a poly-phosphonic acid membrane. The technique is expected to have wider reaching applications in PEM fuel cell and redox flow battery development, as well as in the electrolysis and electrodialysis industries.

1 Introduction

Proton-conducting polymer electrolyte membrane (PEM) materials are widely used in electrochemical devices. The benchmark PEM, Nafion®, contains sulfonate moieties on fluorinated side chains imparting strongly acidic properties to the polymer in its protonated form [1,2]. This acidity is not always desirable for the application; for instance, gas phase electroreduction of CO_2 requires a low proton activity to avoid excess hydrogen evolution [3,4]. Therefore, a large effort is under way to develop new membranes with tailored properties specific to the application. There is, however, no standard measurement technique of the acidity of such membranes.

The concept of pH in a solid polymer electrolyte is challenging to define. Conventionally, pH is defined as $pH = -\log_{10}(a_{H^+})$, where the proton activity, a_{H^+}, is related to volumetric concentration by the activity coefficient, γ, to account for non-ideal behaviour. Thus, in dilute solutions, pH is interpreted in terms of concentration, but this cannot apply in a solid polymer electrolyte. There is nevertheless a need to measure the acidity of such materials. For example, in selecting metallic bipolar plate materials for PEM fuel cells, the local pH between the membrane and the plate determines the rate of corrosion [5–7].

The internal structure of Nafion® has been described [2,8,9], as a network of water-filled channels connecting micellar domains lined with hydrophilic sulfonic acid groups, while the hydrophobic polymer backbone forms a supporting matrix. With increasing membrane humidification, the structure approaches a continuous water phase, which solvates the acidic protons and can conceivably have a measurable pH in the conventional sense. Seger *et al*. [10] attempted to measure the internal pH of Nafion®, using a colorimetric technique by impregnating membranes with methylene blue indicator. They found that the internal pH reflected the presence both of fixed protons, originating from the Nafion® itself, and "labile" protons from the surrounding solution when immersed in solutions of varying pH. In other words, in contafct with an aqueous solution, Nafion® is transparent to pH. However, this paper found the intrinsic proton activity of Nafion®, i.e. the value obtained in contact with ultra-pure water, is equivalent to 1.2 M H_2SO_4 [10].

A separate study using an electrochemical method was performed by Umeda *et al*. [11] who measured the potential difference between a reversible hydrogen electrode (RHE), made from platinum-black on the surface of a Nafion® membrane, and a Normal Hydrogen Electrode (NHE), connected via a glass capillary salt bridge touching the membrane. Their results concurred with those of Seger *et al*., although the authors did not attempt to validate their method with any calibration.

Here we present a simple technique for measuring the proton activity of a PEM. This was developed for screening candidate membranes for a CO_2 electrolysis cell, but the technique will also be useful for other applications. The potential of a pH-sensitive electrode, in contact with the membrane of interest, is measured versus a reference electrode that is insensitive to pH. To demonstrate the measurement technique, a range of membranes was prepared based on Nafion® modified by neutralising the protons with bases such as imidazole and triethylamine. Additionally, hydrocarbon-based cation and anion exchange membranes, and phosphonic acid-containing membranes were studied.

A conventional pH electrode consists of an electrochemical half-cell whose electrode potential depends on pH, measured against a pH-invariant reference electrode. This principle is widely used and understood for aqueous-phase measurements, but is equally valid for solid electrolytes provided a suitable half-cell and reference electrode is used. One option would be to immerse the working electrode/membrane assembly directly in a saline solution containing the reference electrode. However, according to Seger *et al.* [10] this setup would be expected to measure the pH of the chosen solution.

A salt bridge reference electrode design has recently been developed for PEM fuel cells and electrolysers at NPL, UK [12–14], and we have adapted this concept for the present work. The salt bridge consists of a fine tube made of Nafion® and filled with water to ensure maximum conductivity. The reference electrode is placed in a saline solution, into which is immersed one end of the Nafion® tube. The other end is pressed against the membrane of interest, which is cast or compressed onto a dynamic hydrogen electrode (DHE) acting as the pH sensitive electrode.

2 Materials and methods

2.1 pH electrodes

The measurement apparatus is illustrated in Figure 1(a). The membrane sample was placed in contact with a modified commercial screen-printed electrode (Dropsens, Metrohm, France) and mounted in an adapted Flow-Cell apparatus (Dropsens, Metrohm, France) which held the salt bridge in contact with the membrane. The Flow-Cell is marketed as a wall-jet flow cell apparatus, but for the present study the vertical fluid port was adapted to accommodate a Nafion® tube salt bridge (TT-030, Perma Pure, USA) which made contact with the membrane under test. The geometry of the Flow-Cell holds the membrane flat to the surface of the working electrode, with the salt bridge attached to the top side of the membrane in the centre of the electrode area. The other end of the salt bridge sits in a vessel containing 0.1 M K_2SO_4 electrolyte and a saturated calomel reference electrode (SCE). The junction potential of the salt bridge was tested with several buffer solutions and found to be invariant with pH.

Figure 1. (a) Illustration of Dropsens Flow-Cell configuration. (b) Typical potential of DHE under galvanostatic test conditions. (c) Calibration curve of DHE in Flow-Cell apparatus.

The screen-printed electrodes (Dropsens, Metrohm, France) consisted of a gold working electrode (4 mm diameter), platinum counter electrode and silver reference electrode. In this work, since a separate reference electrode was used, the screen-printed silver reference electrode was isolated with acrylic varnish.

The working electrode was platinised according to the method recommended by Feltham and Spiro [15], after first cleaning the gold surface by cyclic voltammetry in 0.1 M H_2SO_4 at 100 mV/s between -0.40 V and +1.36 V (SCE) for 10 cycles. These electrodes were used as DHEs, i.e. generating hydrogen in situ by applying a small current between the platinized working electrode and the screen-printed counter electrode. The current density was controlled at -1 mA cm^{-2} (60 s), -0.2 mA cm^{-2} (60 s) and at open circuit (60 s) in order to account for ohmic and activation overpotentials.

2.2 Selection of membranes for testing

Nafion® N115 was used as a benchmark material for this study, as its proton conductivity and acidity are well characterised. Several studies have been published documenting composite membranes formed by doping Nafion® with molecules containing a basic moiety [16–31]. These were for a diverse range of applications requiring modification of the intrinsic properties of Nafion®, for example as electrolyte membranes in direct methanol fuel cells (DMFC), high temperature PEM fuel cells, and redox flow batteries, as well as for biological applications. Such modification of Nafion® by cation exchange is expected to affect the acidity of the polymer, but this aspect was not considered in the cited studies themselves. Here we have reproduced some of these materials as well as some unrelated ion conducting polymers, as listed in Table 1. All Nafion®-based membranes were prepared from Nafion® N115 (PaxiTech, France) that was first treated by successively boiling for 1 h in 5 wt % H_2O_2; H_2O; 0.5 M H_2SO_4 and again in H_2O, followed by drying at 90 °C in a vacuum oven overnight. The subsequent preparation steps are given in the table. Membranes were fully humidified by soaking in liquid water and dried with tissue paper prior to testing.

The pH response of the electrodes was characterised with calibrated phosphate buffer solutions verified with a conventional pH electrode (Mettler Toledo). After initial testing in bulk solution (not shown here), the electrodes were calibrated in the FlowCell/salt-bridge setup using porous polyamide felt battery separator material soaked in the calibrated buffer solutions. The junction potential of the salt bridge was also assessed and found to be invariant with pH.

Table 1. Membranes used in this study and summary of results

3 Results and discussion

The potential of a DHE vs SCE during a typical experiment is shown in Figure 1(b) (shown for pH 2.13 phosphate buffer), illustrating the initial cathodic reduction of the Pt surface, followed by a steady-state region where hydrogen evolution takes place at a constant rate. The potential becomes less negative when the current density decreases, due to a smaller iR overpotential. Finally, after stopping the current, the open circuit potential (OCP) slowly drifts positive as oxygen diffuses to the electrode surface from the atmosphere.

Figure 1(c) shows the calibration curve, with the OCP values giving a straight line within 1% of the theoretical Nernstian gradient. The most notable feature from the calibration is the offset of the point at pH 7 under -0.2 mA cm^{-2}, compared to the value at OCP, indicating a significant polarisation and/or ohmic overpotential for this buffer solution. This could be due to local depletion of H^+ close to the platinum surface skewing the local pH to higher values, which is a known phenomenon for hydrogen evolution in solutions of neutral pH.

The results of membrane pH measurements are shown in Figure 2. Measurements for each membrane were carried out at least three times to determine the uncertainty of the measurement, and the averaged curve is shown. Each membrane shows the characteristic curve approaching steady state from a positive potential during the -1 mA cm^{-2} stage, changing to a less negative steady state potential during -0.2 mA cm^{-2}, and finally a gradual irregular increase in potential at open circuit. For some membranes (e.g. PS-co-Styphos) the open circuit potential immediately jumps to a less negative value, followed by a more gradual increase. This indicates a high iR overpotential, suggesting a low membrane conductivity. An improved OCP-only technique using a palladium-hydrogen electrode may be possible but palladium electrodes were not available for this work. Nevertheless, repeatable steady state results were obtained for most membranes, with the exception of Nafion® 982 (cathode side – repeatable data could not be obtained) which may be due to the textured woven support structure on the cathode side affecting contact with the electrode; the anode side of Nafion® 982 gave very similar results to H+-form Nafion® 115 (within 11 mV – not shown). The poly(phosphonic acid) membranes (Figure 2b) also displayed erratic results, possibly due to poor lateral conductivity between the working and counter electrodes across the membrane surface.

From these data it can be immediately observed that the hydrogen evolution potential is significantly more negative for the modified membranes. The electrode potentials at OCP for each membrane are summarised in Table 1. These values were obtained by averaging the first 30 s at OCP for each test, and then averaging that value for the three repeat tests. Uncertainty is given as two times standard deviation.

A first simple comparison can be made between the structurally similar polystyrene-based membranes AMI7001 and CMI7000, which are functionalised with a quaternary amine and a sulfonate respectively. Here an alkaline pH is observed for the anion exchange membrane and an acidic pH is observed for the cation exchange membrane. Interestingly, however, the anion exchange membrane does not give as high a pH as might be expected for a pure OH^--conducting electrolyte, possibly due to reaction of atmospheric CO_2 with OH^- to form carbonate.

The results for the modified Nafion® membranes show that imidazole and butylimidazole both have a similar buffering effect on the acidity of Nafion®, with a slightly stronger effect from triethylamine and diethylamine. The difference is likely to arise from the higher pKa of protonated amines (~11) compared to imidazoles (~7). These membranes would be interesting candidates for a CO2 electroreduction cell, which was the main motivation for this study.

Figure 2. Raw data for DHE measurement of several membranes.

4 Conclusions

For the first time, the proton activities of a range of polymer electrolyte membranes have been measured and compared using a straightforward and inexpensive technique. A salt bridge connects the top surface of the membrane under test to a reference electrode, while the bottom surface of the membrane is in contact with a pH-sensitive electrode.

- A platinized-platinum DHE gave good repeatability for ranking the acidity of a range of PEM membranes.
- Membranes based on Nafion® modified by exchanging protons for protonated bases such as butylimidazole or triethylamine were found to have a near-neutral acidity. Further characterisation of these membranes is required to measure the conductivity and the rate of leaching of the molecular species during prolonged operation.
- The novel technique has enabled rapid screening of membranes for use in a PEM electrochemical cell for reduction of CO_2, where near-neutral pH is desirable. The technique will also provide unique

insight into novel membranes for many other electrochemical devices, as well as for understanding corrosion of metallic bipolar plates.

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Figure 1. (a) Illustration of Dropsens Flow-Cell configuration. (b) Typical potential of DHE under galvanostatic test conditions. (c) Calibration curve of Pt DHE electrode in FlowCell apparatus.

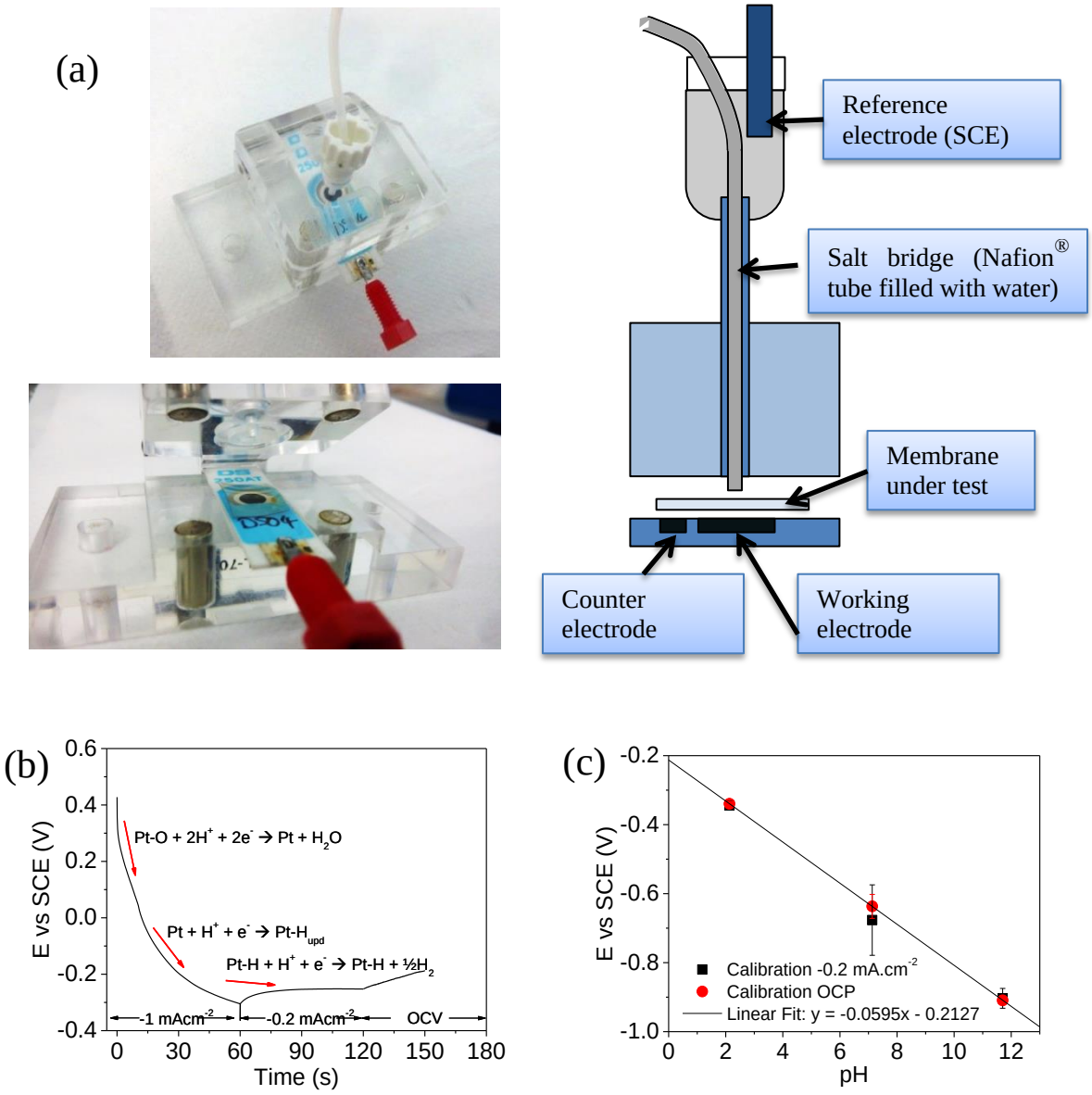

Figure 2. Raw data for DHE measurement of several membranes.

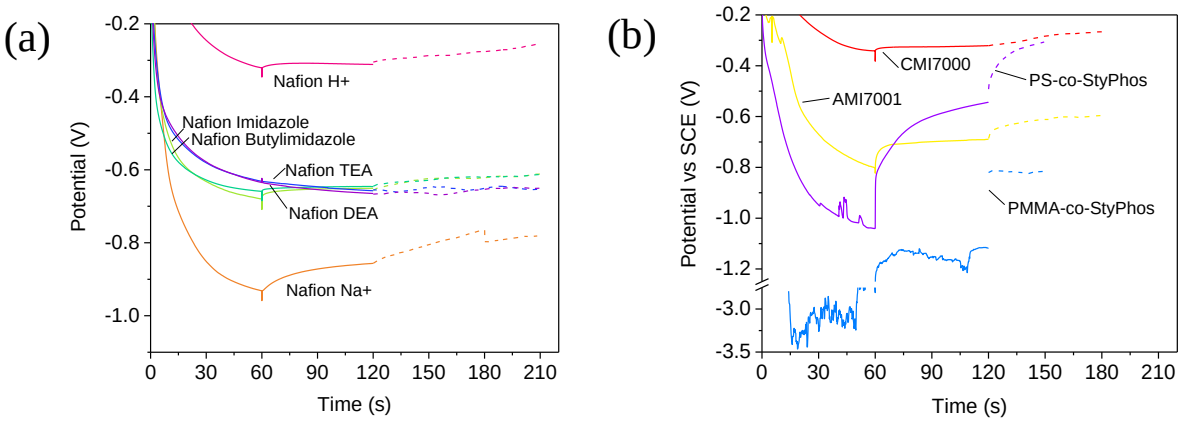

Table 1. Membranes used in this study and summary of results

Membrane name	Preparation method	Ref	Measured E vs. SCE (V)	Calculated pH	Absolute uncertainty in pH
Nafion®(H^+)	N/A		-0.295	1.4	± 0.20
Nafion®(Na^+)	Heat to 80 °C for 1 h in 1 M NaOH (aq), followed by 24 h at room temperature. Then rinse in two successive baths of H_2O at 80 °C for 1 h		-0.849	10.7	± 0.67
Nafion® (Imidazole)	Soak in imidazole–methanol solutions of (a) 0.1 g in 10 mL solution; (b) 2.0 g in 10 mL solution at 55 °C for 2 h, followed by drying in a vacuum oven at 90 °C overnight.	[18]	-0.637	7.1	± 0.40
Nafion® (Butyl-imidazole)	Soak in 1-(*n*-butyl)imidazole–methanol solutions of (a) 0.18 g in 10 mL solution; (b) 3.6 g in 10 mL solution at 55 °C for 2 h, followed by drying in a vacuum oven at 90 °C overnight.	Adapted from [18]	-0.634	7.1	± 0.36
Nafion® (Triethylamine)	Soak in 1 M triethylamine aqueous solution for 24 h at ambient temperature.		-0.656	7.5	± 0.31
Nafion® (Diethylamine)	Soak in 1 M Diethylamine aqueous solution for 24 h at ambient temperature.		-0.663	7.6	± 0.36
AMI7001(OH^-)	AMI7001 (Membranes International, Inc., USA) was soaked in 1 M NaOH for 24 h at ambient temperature to exchange Cl^- ions for OH^-.	[3]	-0.734	8.8	± 0.22
CMI7000(H^+)	CMI7000 (Membranes International, Inc., USA) was soaked in 0.5 M H_2SO_4 for 24 h at ambient temperature to exchange Na^+ ions for H^+.	[3]	-0.325	1.9	± 0.13
PMMA-co-Styphos	Poly(methylmethacrylate-co-styrenephosphonic acid) random copolymer, 9:1 ratio (Specific Polymers, France) was dissolved in DMAc solvent and cast on a porous polyolefin battery separator support.		-0.352	2.3	± 1.45
PS-co-Styphos	Poly(styrene-co-styrenephosphonic acid) random copolymer, 9:1 ratio (Specific Polymers, France) was dissolved in DMAc solvent and cast on a porous polyolefin battery separator support.		-0.822	10.2	± 0.35
Nafion N982	Boil for 2 h in 1 M HNO_3, then rinse in deionized water.	[31]	(Anode side) -0.306	1.6 (Cathode side)	± 0.46
			Unable to produce repeatable result		