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Examination of Amine-Functionalised Anion-Exchange Membranes for Possible Use in the All-Vanadium Redox Flow Battery

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ABSTRACT

The applicability of amine-functionalised anion-exchange membranes (AEMs) for use in the all-vanadium redox flow battery has been studied. A selection of radiation-grafted aminated membranes functionalised with dimethylamine, trimethylamine or diazabicyclo(2,2,2)octane were extensively tested. The success of each grafting process was confirmed by Raman and infrared spectroscopies, titrimetry and ionic conductivity measurements. The amine-functionalised membranes were found to have poor thermo-oxidative stability and high vanadium cation permeabilities. The results highlight the importance of balancing ionic conductivity with vanadium cation permeability and indicate that amine-based functional groups may not be suitably stable for the membranes to remain true AEMs when in use in the all-vanadium redox flow battery.

1. Introduction

Between 2006 and 2030 global energy consumption is expected to increase by 44% [1] and consequently more emphasis is being placed on renewable energy sources and technologies. A major issue in the production of energy from renewable sources is their intermittency. Effective energy storage will allow excess energy (e.g. produced during periods when the wind blows at optimal speeds but where national demand is low) to be stored until it is required (during periods where demand is higher than generation capacity). On "electrification" of the energy chain (introduction of renewable generation and the increased use of electrical heating and electric vehicles), nations will have an energy storage problem in addition to an energy generation problem. Among the many energy storage systems, much attention has focussed on the all-vanadium redox flow battery (VRFB); flow batteries convert electrical energy into chemical energy on charge and *vice versa* during discharge [2].

In VRFBs, two acidic electrolyte solutions containing the electroactive species (redox couples of V^{2+}/V^{3+} and VO^{2+}/VO_2^+) are stored externally and pumped into separated cell compartments when required; the electrochemical cell consists of two electrodes separated by an ion permeable membrane. An advantage of VRFBs is the ability to "decouple" (assuming no vanadium crossover) the energy storage capacity from the power demands of the system; this allows a flexibility in cell design [3,4]. Other advantages include the potential for rapid recharge "hot swapping" and long electrolyte life span (in temperature controlled environments).

The ion permeable membrane physically separates the two electrolytes, ideally preventing self-discharge whilst allowing proton transfer to complete the circuit. It is this requirement of proton transfer that has led to the focus of membrane research for VRFBs to be on cation-exchange membranes (CEMs). The dominant commercial CEM, Nafion, is widely used as the separator membrane in VRFBs due to its perceived excellent chemical stability and high proton conductivity. However, firstly it is expensive (which is a critical consideration as the membrane makes up 41% of the cost of a typical VRFB stack [5]) and secondly, Nafion suffers from high vanadium cation permeability (resulting in lower coulombic efficiency as well as capacity fade during cycling [6–8]). It is this need to balance proton conductivity and vanadium cation permeability that poses the greatest challenge in membrane research for the VRFB application. Anion-exchange membranes (AEMs) may offer a solution – with a better balance between proton conductivity (in the form of H_3O^+) and reduced vanadium cation permeability due to electrostatic repulsion (leading to a supposed Donnan exclusion) between the positively charged functional groups within the membrane and the positively charged vanadium cations [9–11], but that dependent on the AEM retaining its chemical identity and functionality while in use.

In this study a selection of AEMs were prepared by radiation grafting of vinylbenzyl chloride onto ethylene tetrafluoroethylene (ETFE) co-polymer films with subsequent functionalization

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(to introduce the anion-exchange head-groups) using a variety of widely available amines. The intrinsic membrane characteristics were examined using Raman and mid-infrared spectroscopies, titrimetry and electrochemical impedance spectrometry. In order to further examine the applicability of these membranes in VRFBs, properties such as vanadium cation permeability, ionic conductivity and thermo-oxidative stability were determined.

2. Experimental

All chemicals were obtained from Sigma Aldrich and used as received unless otherwise stated. Nafion 115 was pre-treated using the following literature method [12]. Dehydrated membrane was immersed in the following solutions at 90 °C for 1 hour in each, with thorough rinsing with deionised water between each solution change: H_2O_2 (aq, 1 mol dm^{-3}), H_2SO_4 (aq, 1 mol dm^{-3}) and finally deionised water. Brief exposure to peroxide in this standard pre-treatment does not lead to degradation of the treated membrane.

2.1. Membrane Synthesis

The trimethylamine (TMA) AEM method has been widely reported specifically for use in alkaline membrane fuel cells. The methods used in this study (Scheme 1) have been adapted from those previously reported [13,14]. ETFE film (from Nowoflon, Germany, dry thickness of approximately 50 µm) was irradiated in air with an electron beam to a total dose of 7 MRad. The irradiated film was then submerged in a nitrogen-purged solution of the following composition: 20%vol vinylbenzylchloride (VBC, Dow Chemicals, 1:1 meta/para mix), 79%vol propanol and 1%vol Surfadone LP-100 surfactant. The grafting was carried out at 60 °C for 72 hours. The resulting copolymer was immersed in a solution of an amine at 50 °C for 24 hours. Dimethylamine (DMA) and TMA were both supplied as aqueous solutions (40%wt and 45%wt respectively) and were diluted 1:2 with isopropanol to give approximately 20% amine in solution. 20%wt diazabicyclo(2,2,2)octane (*DABCO*) was dissolved in a 1:1 water/isopropanol mix.

2.2. Raman Spectroscopy

Membrane samples were first dried in a desiccator (over $CaCl_2$) for a minimum of 5 days. Raman spectra were recorded on the Perkin Elmer System 2000 FT-Raman/near-IR spectrometer with a laser power of 1400 mW and a resolution of 4 cm^{-1}. Membrane samples were placed in glass vials, folding the membrane so that the laser passed through several layers (thereby enhancing the scattered intensity).

2.3. Mid-Infrared Spectroscopy

Membrane samples were first dried in a desiccator (over $CaCl_2$) for a minimum of 5 days. Infrared spectra were collected using the Perkin Elmer Spectrum BX FT-IR Spectrometer. Dry membranes were studied using the Specac Mk II Golden Gate ATR attachment containing a diamond 45° ATR window and a sapphire anvil. Each membrane was subjected to 32 repeat scans over the range 600–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

2.4. Through-Plane Ionic Conductivity (IC)

To determine the membranes' conductivity, electrochemical impedance spectrometry was used. The membrane sample was soaked in H_2SO_4 (aq, 1 mol dm^{-3}) overnight and then mounted between two graphite plates within a high density polyethylene cell. The conductivity cell was held together, under constant torque, using two securing screws and was suspended in H_2SO_4 (aq, 1 mol dm^{-3}) at ambient temperature (20 - 22 °C). The impedance spectra were collected on the Solatron 1260/1287 frequency gain analyser with maximum voltage amplitude of 100 mV and a frequency range of 1 kHz–1 MHz. Each membrane was investigated five times. The conductivity of the membrane is determined by the Nyquist plot where the x-axis intercept is the resistance. Conductivity (σ, S cm^{-1}) is calculated using Equation 1, where t is hydrated membrane thickness (cm), R is resistance (ohm) and A is geometric contact area (cm^2).

$$\sigma = \left(\frac{t}{R \times A}\right) \qquad \text{(Equation 1)}$$

2.5. Gravimetric Water Uptake (GWU)

Membrane samples were dried for a minimum of 5 days in a desiccator over $CaCl_2$. The gravimetric water uptakes (GWU) were determined by measuring both the hydrated and dehydrated masses of the membrane, using a calibrated five figure balance (Sartorius AG, CP225D-OCE). GWU (%) is calculated using Equation 2 where m is either the hydrated or dehydrated mass (g) of the membrane sample.

$$GWU = \left(\frac{(m_{Hyd} - m_{Deh})}{m_{Hyd}}\right) \times 100\% \qquad \text{(Equation 2)}$$

2.6. Ion Exchange Capacity (IEC)

The IEC is a measure of the number of ionic sites that can participate in an exchange process and is expressed in mmol g^{-1}(dehydrated membrane). During the methods described below the membrane was rinsed with deionised water, until the washings were pH 7, to ensure repeatability.

To measure the IEC of the AEMs, a back titration method was employed where the membrane was first soaked in KOH (aq, 1 mol dm^{-3}). The membrane was rinsed thoroughly with deionised water and then soaked in HCl (aq, 1 mol dm^{-3}) for at least 3 hours, stirred at 350 rpm. The membrane was thoroughly rinsed with deionised water and then soaked in $NaNO_3$ (aq, 1 mol dm^{-3}, approximately 30 cm^3) overnight with stirring (350 rpm). The membrane was again thoroughly rinsed with deionised water (washings going into the vessel containing the $NaNO_3$) and approximately 2 cm^3 of HNO_3 (aq, 1 mol dm^{-3}) was added. The resulting solution was titrated with $AgNO_3$ (aq, 0.02 mol dm^{-3}) using a Metrohm 848 Titrino Plus with a conductivity probe. The end point was determined via the maxima in the differential curve (d(conductivity)/d(volume $_{\text{titrant}}$)). This procedure was conducted three times for each membrane, and a blank (membrane-free) was run with each batch, consisting of a known volume of HCl (aq, 1 mol dm^{-3}, 2 cm^3), HNO_3 (aq, 1 mol dm^{-3}, 2 cm^3) and sufficient deionised water to facilitate the conductivity probe. The IEC was calculated using Equation 3 where n is the amount (mmol) of silver ions and m_{Deh} is the dehydrated mass (g) of the membrane.

$$IEC = \frac{n}{m_{Deh}} \qquad \text{(Equation 3)}$$

To measure the IEC for CEMs, the membranes were first soaked in H_2SO_4 (aq, 1 mol dm^{-3}) overnight whilst being stirred at 350 rpm and then rinsed thoroughly with deionised water. The membrane was then soaked in approximately 20 cm^3 of NaCl (aq, 1 mol dm^{-3}) solution and stirred at 350 rpm overnight. The membrane was thoroughly rinsed with deionised water (washings going back into the vessel). The solution was then titrated with HCl (aq, 1 mol dm^{-3}) using the Metrohm 848 Titrino Plus with a pH probe. This procedure was repeated three times for each membrane and a blank was run with each batch, consisting of 1 cm^3 of HCl (aq, 1 mol