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Cationic diodes by hot-pressing of Fumasep FKS-30 ionomer film onto a microhole in polyethylene terephthalate (PET)

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ABSTRACT

A cationic diode is fabricated by hot-pressing a commercial cation-conducting ionomer membrane (Fumasep FKS-30) onto a polyethylene terephthalate (PET) substrate with microhole of 5, 10, 20, or 40 μm diameter. Both, symmetric (ionomer on both sides) and asymmetric (ionomer only on the working electrode side) cases are investigated in a 4-electrode measurement cell. A 5-electrode measurement cell in generator-collector mode is employed to directly detect competing proton transport through the ionomer. Only the asymmetric device allows ion current rectification to be observed. With decreasing microhole diameter the rectification effect increases. With increasing electrolyte concentration (for aqueous HCl, NaCl, LiCl, NH_4Cl, $MgCl_2$, $CaCl_2$) the rectification effect diminishes. Competition between cation transport and proton transport is observed in all cases. A qualitative impedance model is developed to diagnose the quality and performance of these cationic diodes.

1. Introduction

Ionomer films are routinely applied in membrane materials, which are crucially important in many areas of electrochemistry including fuel cells [1], electrosynthesis [2], and in desalination devices [3]. Semi-permeable ionomer films (such as those based on Nafion [4–6]) are widely used and have recently been shown to also allow ionic current rectifiers to be designed [7]. The function of these ionic current rectifiers has been modelled [8] and suggested to be linked to both local concentration/conductivity changes and polarisation at the ionomer | electrolyte interfaces. These ionic current rectifiers or ionic diodes could have potential for application in “iontronics” [9] or in ionic energy conversion [10,11]. Recently, a wider range of ionomer film materials attached to a poly-ethylene-terephthalate (PET) substrate with a microhole have been shown to exhibit ionic rectification effects, which lead to “ionic diode” behaviour. For cation-conducting cellulose films [12] “cationic diode” phenomena were demonstrated, and for polymer of intrinsic microporosity (PIM) films pH-switchable diode phenomena were reported [13,14]. These ion current rectification effects could be of interest in polymer or cellulose-based water purification and desalination [15], but possibly also in energy conversion [16] and in sensing [17]. Therefore, it is interesting to explore ion transport and rectification phenomena as a function of ionomer material and of diode geometry. In contrast to studies with drop-cast ionomer materials, more defined ionic diode geometries are possible, for example, by hot-pressing ionomer film of defined thickness onto a PET support film with microhole.

Ionic diode or ion current rectification effects are associated with the ability of ion channels to undergo structural changes under applied voltage bias. Many examples are known for nano-channel diodes [18,19] in which double layer and compositional changes create localised depletion/accumulation effects leading to “closed” and “open” diode behaviour. Bockris reported electrolytic diodes [20], which rely on the formation of ion depletion and ion accumulation zones. Today, a wider range of electrolytic rectifiers is known [21] and novel diodes based, for example, on asymmetric permselective membranes [22] and on chemical precipitation reactions [23] have been reported. If properly understood, developed, and optimised, the ability of ionic diodes to allow or inhibit ions to pass through could be used as a separation technique to treat wastewater and to selectively remove some toxic

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heavy metals and/or anions from waste streams.

This study aims to introduce hot-pressing as a technique for fabricating ionic diodes with defined geometric dimensions from commercial Fumasep FKS-30 ionomer films and poly-ethylene-terephthalate (PET) substrates. The hot-pressing method offers a better defined ionic diode geometry, when compared to the conventional solution drop-casting and drop-drying of ionomer films on PET [24]. Fumasep FKS-30 ionomer membranes are employed here as cation conducting membranes [25]. Reported properties of Fumasep FKS-30 ionomer films are high permselectivity and an ion exchange capacity (IEC) of 1.3 to 1.4 meq/g dry membrane [26]. This corresponds to an equivalent weight of 1 / IEC = 740 Da close to that reported for Nafion ionomer materials. The water transference associated with cation transport in Fumasep FKS-30 has been investigated [27]. There is also a recent report on the application of Fumasep membranes in desalination technology [28]. It is shown here that hot-pressing allows cationic diodes to be fabricated and that the resulting rectification phenomena are dependent on microhole diameter, electrolyte concentration, and the nature of the electrolyte. Significant competition of cation transport with proton transport is observed.

2. Experimental

2.1. Materials

Poly-ethylene-terephthalate (PET) films of 6 µm thickness with laser-drilled micropores (of nominally 5, 10, 20 and 40 µm diameter) were obtained from Laser-Micro-Machining Ltd., Birmingham UK, and used as substrates for fabricating cationic diodes with Fumasep FKS-30 (nominally 30 µm thickness, Fuelcellstore.com) as the ionomer film. All the reagents used for preparing the solutions were analytical or reagent grade and were purchased from Sigma-Aldrich (UK).

2.2. Instrumentation

The ionic diodes were fabricated using a Swing Away heat-press machine (HP230B, Amazon, UK). All electrochemical measurements were recorded either using an Autolab potentiostat (GPSTAT, Eco Chemie, NL) or using a Solartron 1286/1250 potentiostat/analyser combination in a conventional four-electrode configuration (see Fig. 1) and by employing a measurement cell based on two electrolyte-filled half-cells separated by the membrane [13]. One half-cell contains the Pt wire working electrode and a saturated calomel (SCE) sense electrode and the other half-cell contains the SCE reference and Pt wire counter electrodes. In some experiments a second working electrode is introduced (in the five-electrode configuration, see below) to monitor proton transport through the diode.

2.3. Procedures for membrane fabrication

To form an asymmetric diode, a 1 cm^2 piece of Fumasep FKS-30 film was cut out and placed on top of a PET film (covering the microhole). The assembly was sandwiched between two Teflon films followed by hot pressing on a preheated hot-press (180 °C) for 45 min. To form a symmetric diode a procedure like the one used above, however, two 1 cm^2 Fumasep FKS-30 pieces are placed opposite to each other with the PET film sandwiched, followed by hot-pressing between two Teflon films for 45 min. Ionic diodes obtained in this way are reasonably robust, but weak adhesion between ionomer and PET does cause occasional delamination, particularly at higher applied potentials. Therefore, applied potentials in this study are limited to ± 2 V.

Fluorescence imaging experiments were performed on a Carl Zeiss Confocal Scanning Microscope. A Fumasep FKS-30 film was soaked for 5 h in a dilute rhodamine B solution (*ca.* 0.1 mM in water), after which the film was rinsed thoroughly and dried at 50 °C in an oven. The (partially) dyed film was then hot-pressed on PET as previously described, and placed on a glass substrate for fluorescence imaging (Fig. 1).

3. Results and discussion

3.1. Assembly of symmetric and asymmetric membrane architectures

Hot-pressing was selected as a convenient process for producing ionic diodes based on approximately 1 cm^2 pieces of Fumasep FKS-30 (nominally 30 µm thickness) and a 5 cm × 5 cm PET substrate (6 µm thickness) with central microhole (typically 20 µm diameter). The temperature was increased to improve adhesion and after optimisation 45 min of 180 °C was selected for “asymmetric” films. For “symmetric” membranes the Fumasep FKS-30 ionomer was placed both below and above the PET substrate. Fig. 1A shows a multi-stack fluorescence microscopy image as top view (with focus on the PET layer) and as side view. The rhodamine B dye (only used here for fluorescence microscopy) can be seen to have penetrated only partially (*ca.* 5 µm deep) into the Fumasep FKS-30 films therefore giving fluorescent layers at the location of the ionomer surfaces. Fig. 1A shows the symmetric membrane assembly with the PET substrate in the middle. The top view shows the approximately 20 µm diameter microhole, but also some PET

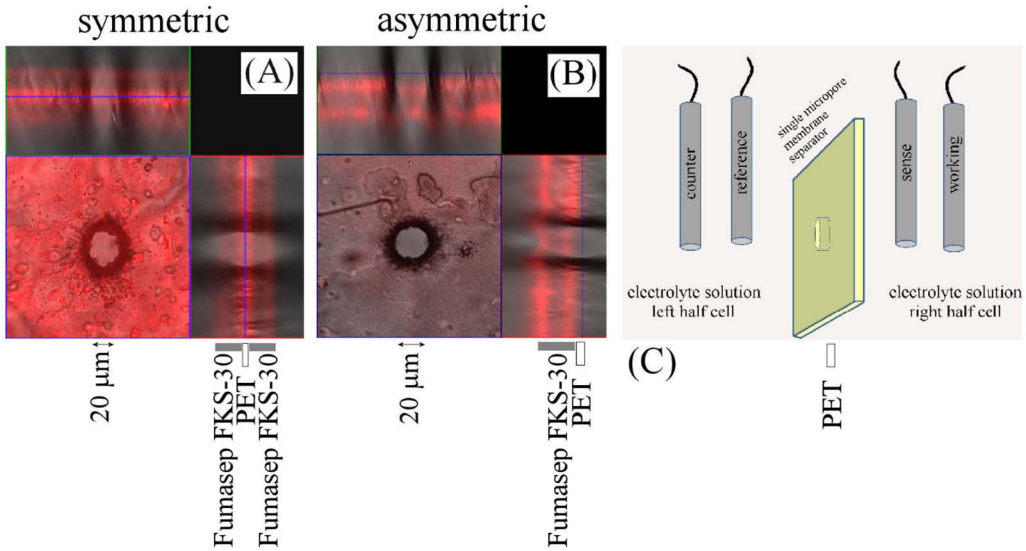

Fig. 1. Confocal microscopy image (fluorescence from rhodamine B dye partially adsorbed into the surface of the Fumasep FKS-30 film) for (A) a symmetric device with Fumasep FKS-30 on both sides of the PET film and (B) an asymmetric device with Fumasep FKS-30 only on one side. (C) Schematic drawing of the 4-electrode configuration for membrane voltammetry and impedance with ionomer films always on the side of the working electrode.