

Ion Transport in Polymer Composites with Non-Uniform Distributions of Electronic Conductors



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ABSTRACT

Ionic resistance is often a rate limiting factor in electrochemical systems such as batteries, supercapacitors, and ionic polymer actuators. Such cells typically contain laminated and interpenetrated structures consisting of one or two electronically conductive layers and an ionically conductive separator layer. Here we analyze the role of electrodes in determining ionic resistance, and study the effects of interpenetrating ionic and electronically conducting phases. We also show that conducting polymer electrodes that are polymerized on separator layers, as have been applied to create actuators, supercapacitors and electrochromic device, can be widely and unevenly distributed through the device. Swept sine and DC measurements are used with a four-point diffusion cell probe to characterize the phase dependent ionic impedances in 1. polypyrrole (PPy) coated polyvinylidene fluoride (PVDF) and 2. poly(ethylene dioxythiophene) (PEDOT) interpenetrated poly(ethylene oxide) (PEO) – nitrile butadiene rubber (NBR) co-polymer with various PEDOT content levels. A finite Warburg-based model is introduced to explain the frequency dependence, enabling a time constant for ion transport within membrane to be estimated. It is found that the separator layers in the composite membranes are shorted at higher frequencies (10~100 Hz). This effect is likely due to interpenetration of the electronic phases into the bulk of the separator layers, providing a means of reducing internal resistance and increase power at short times. Finally, a non-uniform impedance distribution model is introduced to predict the effective composite ionic conductivity in terms of the ionic conductivities of each phase, and their non-uniform volume fractions. Taken together, the approaches presented provide a means of probing the influence of ionic conductivities of various phases on the rate of charging in electrochemical devices.

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1. INTRODUCTION

Multilayered, heterogeneous ion conductors are employed in various applications such as batteries [1–3], fuel cells [4], supercapacitors [5–9], ion exchange membranes [10], and conducting polymer based devices [11–16]. For example, supercapacitor electrodes typically consist of high surface area and electronically conductive carbon particles held together by a polymer binder. The macroporous region around the carbon

particles allows ions to travel long distances with relatively high ionic mobilities. However, as electrodes get thicker, at some point the ionic resistance between conducting particles can be a rate limiting factor in charging. The thicknesses and morphologies of the electrodes and of the separator are factors in determining the device charging speed and current density [17,18]. In modeling and optimizing such structures, particularly to increase energy and power capacities, an understanding of ionic conductivities in each of the ion conducting phases is useful. In this paper (1) the impedance of multilayered and interpenetrating structures is characterized, including both ionically and electronically conductive phases; (2) we propose a physical model to describe the transport of ions in films that are both ionically conductive and pseudo-capacitive (containing conducting polymers), and; (3) the ionic conductivity of a non-uniform distribution of ionic and

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electronically conductive phases is simulated and matched to empirical data via a distributed model incorporating local ratios of each phase.

The two-electrode AC measurement method, which clamps a specimen between inert metal plates, is often used to determine ionic conductivity of a membrane. However, it is not generally useful when the membrane contains electronically conductive phases. The four-electrode configuration in a diffusion cell, as seen in Fig. 1, has previously been applied to describe the ion transport in mixed electronically and ionically conducting membranes. Placing the specimen under a solution/membrane/solution boundary condition (by driving ionic current through the entire structure) makes it possible to decouple the electronic and ionic contribution to charge transport as a function of frequency. Burgmayer and Murray [19,20], Ehrenbeck and Jüttner [13,21,22], Otero et al. [23], and many others [24–30] have used this approach to investigate ion transport in polythiophenes, polypyrrole and other conducting polymers as a function of oxidation states or doping conditions. Most of this work has investigated the impedance at low frequencies and/or the step current response to extract the ionic resistance of the membrane under study. Such characterizations were motivated for example by the potential use of conducting polymers as switchable ion gate membranes [19]. Heterogeneous polymers such as polypyrrole/polystyrenesulfonate [27] and polypyrrole/graphene oxide [28] have been investigated, although little work has been done to predict the trend in ionic conductivity as a function of the relative composition of these materials.

In this work, the four-point approach is used to measure the ionic conductivity of two types of heterogeneous composites: (1) polypyrrole coated polyvinylidene fluoride (PPy/PVDF), and (2) poly(3,4-ethylenedioxythiophene) interpenetrated poly(ethylene oxide) – nitrile butadiene rubber co-polymer (PEDOT/PEO-NBR). Polypyrrole coated PVDF membranes are used to create bending actuators and mechanical sensors [31]. In the actuators, one side of the electrolyte filled membrane is oxidized electrochemically, while the other is reduced, leading to ion transfer between the two. The ion transfer is associated with expansion on the receiving side,

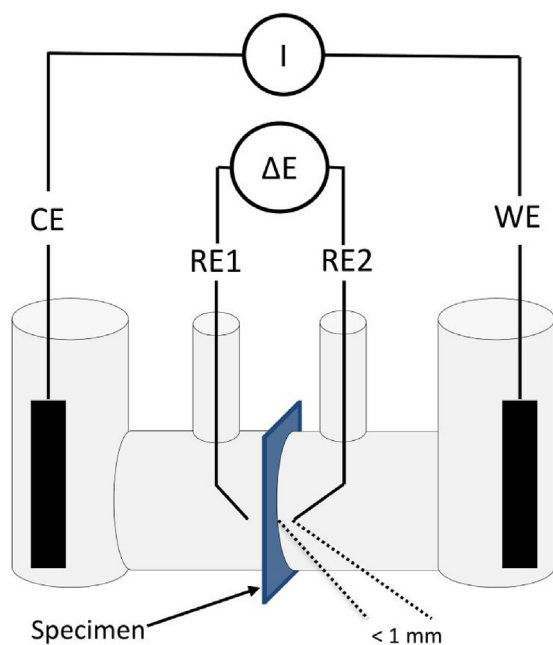


Fig. 1. The diffusion cell experimental set-up. The potential difference is measured across the reference electrodes while a current perturbation (DC or swept sine) is applied between the counter and working electrodes.

and contraction on the donating side, resulting in net bending. Conversely, voltages and currents are generated when the beams are deflected. Interestingly, the bending sensitivity rolls off at low frequencies – perhaps due to weak electrical connectivity between the two electrodes, as discussed in this paper. PEO-NBR is one of several interpenetrated polymer networks (IPNs) that have attracted attention due to their high ionic conductivities (resulting from an electrolyte swollen PEO phase) and their combination of low modulus and large elongation at break [32,33]. PEDOT and other conducting polymers can be interpenetrated by polymerizing *in situ*, which tends to grow the polymer inward from the membrane surfaces, forming an electrode at each interface. These two electrode structures have been applied to create electrochemically driven artificial muscle, supercapacitors and electrochromic windows [34,35]. Remarkably, operation at 900 Hz has recently been demonstrated [36]. The shorting effect observed in the work presented here may help explain the fast response, as the relatively high ionic resistance of the separator is bypassed.

In addition to the high frequency bypassing of the separator layers in PPy/PVDF and PEDOT/PEO-NBR cases, we also present an impedance model to enable interpretation of the complex impedances obtained in combined ionically and electronically conductive regions of IPN electrodes. This model includes a RC transmission line impedance, as depicted in Fig. 2(b). The time constant associated with this transmission line is given by the product of the ionic resistance within the electrode and the effective capacitance. The magnitude of this time constant can help determine whether the ionic resistance of the electrode is the rate limiting factor and can provide insight on how to change the electrode design in order to reduce charging time.

The PEDOT electrodes are found to be most dense near the surfaces of the membranes and to drop off sharply in the middle of the structures. As PEDOT has higher ionic resistivity than the PEO-NBR, we model the effective ionic conductivity of these regions based on estimates of their relative volume fractions, as characterized via energy dispersive x-ray spectroscopy (EDX). This is an extension of previous work describing ion transport in heterogeneous electrodes, which has assumed a uniform distribution of the phases. For example, Fekri et al. measured ionic conductivity in carbon fibre paper into which various amounts of polypyrrole were electrodeposited. A model was generated to estimate the upper and lower bounds of ionic conductivity as a function of polypyrrole content, based on the assumptions that the impedances of each phase added in series (lower bound) or acted in parallel (upper bound) [37]. In our work, the model is a hybrid series-parallel combination that accounts for the gradient in conducting polymer volume fraction within the sample. In general, the method should be useful for those wishing to estimate the influence of electrode composition on speed of charging.

2. EXPERIMENTAL

Heterogeneous ionically conductive composites based on polyvinylidene fluoride electrodeposited with polypyrrole (PPy/PVDF/PPy) and poly(ethylene oxide) – nitrile butadiene rubber interpenetrating polymer network with various levels of oxidatively polymerized poly(ethylenedioxythiophene) (PEDOT/PEO-NBR/PEDOT) have been synthesized and characterized. Since actuation speed is often limited by the rate of ion transfer into the polypyrrole layer, it is useful to characterize the ionic conductivity within each layer of this laminate. The second structure tested is the PEDOT/PEO-NBR/PEDOT interpenetrating polymer network with various PEDOT concentrations (0, 5, 12, 19, 25, and 26 wt.%). In this case, the electroactive polymer PEDOT is polymerized *in situ* within the host PEO-NBR copolymer matrix and thus the ion conduction mechanism differs from specimens

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