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Ion transport in polymer composites with non-uniform distributions of electronic conductors

Yuta Dobashi
University of British Columbia, Canada

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.

yuta.dobashi93@gmail.com