Influence of porosity on charging speed of polypyrrole

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ABSTRACT

The rate of charging of supercapacitor and battery electrodes is often limited by the transport of ions through the active electrode material. One way to accelerate this transport is to increase the porosity of the electrode, at the cost of electrode capacity. This tradeoff is studied through the fabrication and characterization of porous carbon nanofibre/polypyrrole films used as storage electrodes. Electrospun poly (acrylonitrile-co-acrylamide) fibres were carbonized and then electrochemically coated with variable amounts of polypyrrole. The resulting hybrid materials were characterized using both conventional methods such as cyclic voltammetry, electron microscopy and conductivity, as well as ionic conductivity and pulsed-field-gradient nuclear magnetic resonance which directly probe ion transport. It is found that with modest porosity, these materials retain much of the capacitance (∼50%) of bulk polypyrrole with dramatically increased (∼300 times) charge and discharge rates, suggesting the potential of the approach for increasing the useful frequency range of polypyrrole-based supercapacitors, as well as other storage materials whose porosity can be varied. Simple transport models based on series or parallel arrangements of electrolyte and active electrode are developed to explain the results and identify the factors limiting charge/discharge rates.

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1. Introduction

Increasing energy density has been a key objective of materials research on batteries and supercapacitors. In many applications, power density is equally important. For example, electrical double layer capacitors, other supercapacitors, and batteries often do not have the power density needed to directly drive a camera flash, to provide current pulses needed in wireless communications, or to provide the short term power bursts needed to maintain power quality for grid-connected devices.

How can power density be improved in electrochemical devices, and is there a tradeoff between power density and energy density? Mass transport limitations within electrodes can in principle be overcome by reducing electrode thickness. Generally the time constant associated with mass transport within a storage electrode is proportional to the square of the diffusion or migration distance. However, attaining very short diffusion time constants by using thin electrodes has some drawbacks. To maintain the same capacity the overall electrode area must be increased, requiring additional backing and separator area, which reduces the device volumetric

capacitance. Furthermore, thinner electrodes can be mechanically delicate, making assembly a challenge. If separators and conducting backing layers are made thinner in order to maintain energy density, then these also can become harder to manage.

As an alternative to creating thinner electrodes, electrodes can be made more porous in order to produce faster charge and discharge. A phase enabling fast ion transport can be interspersed with a slower phase that enables storage. Transport distances into the storage phase are thus short. There are many examples of such fast electrodes, including graphite and amorphous carbon electrodes used in supercapacitors and lithium ion batteries, as well as carbon nanotube and graphene based electrodes, some of which show very fast response [1,2]. The tradeoff is that while increased porosity leads to faster charge transfer, lower volumetric storage density is expected as the volume fraction associated with storage is decreased.

Polypyrrole (PPy) and other conducting polymers have long been known to have very high volumetric and gravimetric effective capacitance ($\sim 2 \times 10^8$ F/m^3, >100 F/g [3]), combined with a relatively wide potential range over which this behaviour is observed (e.g. 1.4 V [4]). However, it is generally not porous, with ions forced to squeeze into the polymer structure itself [5]. The dense structure leads to slow charging for electrodes that are tens of micrometres thick, typically on the order of minutes [6]. In order to achieve fast

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charging, short transport paths are needed. For example, second to sub-second responses are achieved in micromachined devices with ~400 nm thick films [7,8]. If ions were as free to move in the polymer as they are in electrolyte, the charging could be approximately 10,000 times faster, based on the relative ion conductivities measured in this study (0.18 S/m electrolyte, <10^{-5} S/m polymer). A porous electrode that is 10 μm thick could then charge as quickly as a bulk PPy electrode that is 100 nm thick.

A number of efforts have focused on creating porous polypyrrole. For example, by employing potentiodynamic deposition, granular and porous polypyrrole can be electrodeposited, which results in high gravimetric capacitance polypyrrole, and charging within seconds [9]. The use of a porous template and conductor has been shown to produce good power densities (12 kW/kg) in conducting polymer coated electrodes [10]. Polypyrrole nanofibres combined with carbon nanotubes [11] and nanotubes on nickel foam [12] have also been studied. Despite these and many other studies of capacitance and charging rate in porous polypyrrole electrodes, we are not aware of work in which the effect of a wide range of porosities is investigated in order to determine the trade-offs between rate and capacitance.

Here the enhancement in response rate seen in porous PPy as a function of porosity is investigated. PPy is a virtually insoluble polymer, so in order to introduce porosity a conducting scaffold is used upon which the electroactive polymer is deposited. The approach is similar to that of Izadi-Najafabadi et al. [13], in which carbon fibres were used as the scaffold, except that in this case the fibres are much smaller in diameter (0.4 μm diameter rather than 8 μm). The PPy coatings are correspondingly much thinner in the present results in order to allow faster charging.

The polypyrrole deposition method employed (low temperature, galvanostatic at low current density [14]) is well established and the resulting polymer well-characterized. Polypyrrole electronic conductivity is high (100–1000 S/cm [15]) as a result of the ordered structure produced by the low temperature and slow deposition [16,17], dropping by a factor or 100 or more when reduced towards the neutral (undoped) state [18]. As grown the polypyrrole contains one dopant ion (hexafluorophosphate) for every 3–4 monomers [15,19]. We find Brunauer–Emmett–Teller based surface area to be negligible in these dense and highly ordered polymers.

Conventional electrochemical characterization of the porous electrodes is supplemented with two powerful techniques, ionic conductivity and pulsed-field gradient nuclear magnetic resonance (PFG-NMR), to quantify the effect of porosity on transport. Direct measurements of the ionic conductivity are made using a 4 probe technique that works in electronically conductive materials [20–22] and are successfully described with a transmission line model. PFG-NMR diffusion measurements reveal two diffusion coefficients associated with the composite electrodes, one corresponding to the electrolyte phase, the other to the PPy layers.

It is shown that substantially faster charging can be achieved in porous electrodes, with only a modest penalty on volumetric capacitance. The results and analysis show that introducing moderate porosity to the electrodes shifts the rate-limiting factor for device charge/discharge speed from the electrodes to other device components, i.e. the separator. A strategy for producing faster separators with a similar electrospun scaffold is discussed.

2. Experimental

Polypyrrole films and coatings were grown electrochemically following a procedure similar to that of Yamaura [14]. Galvanostatic deposition (SI 1287, Solartron Analytical, Hampshire, UK) was performed from a solution of 0.06 M distilled pyrrole (Sigma–Aldrich, Oakville, Canada), 0.05 M tetrabutyl ammonium hexafluorophosphate (TBAP) (Sigma–Aldrich), and 1 vol% distilled water in propylene carbonate (PC) (Sigma–Aldrich). The solution had been bubbled with nitrogen to deoxygenate it before deposition. Polypyrrole films were grown onto a glassy carbon cylinder with an encircling copper sheet as the counter electrode. A constant current density of 0.125 mA/cm^2 was used for 8 h at a temperature of −35 °C, resulting in ~14 μm thick films, with about 20% variation in thickness over the cylinder surface. Hybrid CNF/PPy films were prepared by immersing ~1.5 × 2.5 cm sheets of carbon nanofibre paper into the deposition solution with similarly sized sheets of carbon paper (AvCarb T75, Lowell, MA) placed in the solution to either side as counter-electrodes. Deposition times of 3, 4, 6 and 8 h were used to produce films with porosities in the range of 44–81%. A bulk PPy film and an undeposited CNF sheet were taken to represent the minimum (0%) and maximum (91%) possible porosities. A full description of the preparation and characterization of the CNF sheets can been found elsewhere [23,24]. Briefly, 10% solutions of co-polymerized acrylonitrile/acrylamide (132:1) were electrospun in a nanofiber electrospinning unit (Kato Tech Ltd., Kyoto, Japan) with a potential of 10 kV. The electrospun polymer fibres were carbonized in a Thermolyne 79400 tube furnace (Thermo Scientific, Waltham, MA) at 1100° for 1 h.

The films' porosities, or void volume fractions, were estimated using the initial masses and density (1.9×10^6 g/m^3 [25,26]) of the carbon nanofibres along with estimates of the mass and density of PPy deposited. The estimated mass of deposited PPy was based upon the integrated deposition current, allowing for the incorporation of PF_6^- ions in the film at a level of one ion per four pyrrole monomers [19,27,15,28]. The dry PPy density was taken to be 1.5×10^6 g/m^3 [29].

Scanning electron microscopy (SEM) images were collected with an Hitachi S-3000 SEM. The samples were conductive enough that no conductive coating was required.

Electrical conductivity measurements were made on air-dried samples by pressing four parallel, equally spaced gold wires against the sample surface, then using the 4-wire resistance mode of an HP 34401A multimeter (Agilent Technologies, Santa Clara, USA). Sample dimensions were measured by hand with a micrometre.

Cyclic voltammetry (CV) measurements were made in a three-electrode 0.1 M TBAP/PC cell using the Solartron 1287A Electrochemical Interface in potentiostat mode with a carbon-fibre paper counter electrode and an RE-4 Ag/AgCl reference electrode (BASi Labs, West Lafayette, USA). The sample masses used in calculation of specific capacitance were the same as those used in the calculation of porosity, above. These mass estimates include the mass of embedded PF_6^- ions, and so underestimate the true specific capacitance of the uncharged materials.

Ionic conductivity measurements were made in a home-built apparatus [20,21] similar to that described by Ehrenbeck and Jüttner [22]. Two symmetric, electrolyte (0.1 M TBAP/PC) filled sides of a glass cell sandwich a 1 cm diameter circular portion of the membrane under test. Stainless steel electrodes ~2 cm on either side of the membrane are used to generate an ionic current through the membrane (driven by the SI1287A). The potential difference across the membrane is measured using RE-4 electrodes protruding through sharp-tipped nozzles positioned close (2.5 mm) to the film surfaces. Measurements were made with a current of 0.005 or 0.1 mA in amplitude. In order to separate the solution contribution to the ionic resistance from that of the membrane, measurements are repeated with the film removed and the two glass sides pressed together.

Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) measurements of ion diffusion coefficients were made on a home-built NMR spectrometer [30] based upon an 8.4 T, 89 mm bore Oxford Instruments superconducting magnet (Oxford, UK).