Understanding Ionic Transport in Polypyrrole/Nanocellulose Composite Energy Storage Devices

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Abstract

In this work, we aim to resolve different diffusion processes in polypyrrole/cellulose composites using a combination of impedance spectroscopy and finite element simulations. The computational model involves a coupled system of Ohm's law and Fickian diffusion to model electrode kinetics, non-linear boundary interactions at the electrode interfaces and ion transport inside the porous electrodes, thereby generating the impedance response. Composite electrodes are prepared via chemical polymerization of pyrrole on the surface of a nanocellulose fiber matrix, and the electrochemical properties are investigated experimentally using cyclic voltammetry, impedance spectroscopy and galvanostatic cycling. It is demonstrated that the onset frequency of the capacitive (or pseudocapacitive) process depends on the counter ion electrolyte diffusion, which is modulated by adding different amounts of sucrose to the aqueous electrolyte solution. Consequently, the electrochemical properties can be controlled by diffusion processes occurring at different length scales, and the critical diffusion processes can be resolved. It is shown that under normal operating conditions of the the limiting process for charge transport in the device is diffusion within the electrolyte filled pores of the composite electrode.

Keywords: Polypyrrole, Charge transport, Impedance spectroscopy, Finite element methodology

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1. Introduction

Electronically conducting polymers such as polypyrrole (PPy) or polyaniline (PANI) have been found to have relatively high theoretical capacities ranging from approximately 100 to 140 mAh g⁻¹, due to that (mainly) Faradaic and capacitive currents both contribute to the charge storage [1–6]. The transport phenomena in conducting polymers, now commonly recognized as potential device material for flexible energy storage devices, sensors and ion exchange membranes [7–10] have been increasingly studied during the last few years, not least by ac impedance spectroscopy. The physical and chemical phenomena behind the impedance response are, however, often a superposition of various effects on different time and length scales which can be difficult to resolve. In this context, electrochemical modelling techniques can contribute to understand the fundamental processes. This, in turn, require model development beyond the common equivalent circuit approximations toward physical-electrochemical descriptions in order to fundamentally assess the origins of the complex chemical processes involved and improve the level of accuracy.

Conducting polymers consist of conjugated chains with the possibility to be oxidized (p-doping) and/or reduced (n-doping) under simultaneous counter-ion diffusion in the polymer matrix. The conductive properties arise in the p-doped or n-doped state, where the electron deficiency or excess can move on the polymer chain or hop between chains through rearrangement of the electron distribution[11]. Since a single conducting polymer chain can undergo several oxidation/reduction processes several times, conducting polymers generally do not exhibit one single redox potential but a range of overlapping signals, thereby generating a supercapacitive electrochemical response[12, 13].

Conductive PPy/cellulose composites can be prepared within 30 min at room temperature and in aqueous solution, by chemical polymerization of pyrrole in the presence of dispersed Cladophora nanocellulose fibers [14–16]. The cellulose will provide a stabilizing matrix for the resulting composite has high surface area (80m²/g), is free-standing and mechanically flexible. Additionally, the 100 nm thin layers of PPy yield short mass transport distances and prevents cracking as a result of volume expansion during redox conversion, which renders greatly improved cycling stability[17]. Symmetric energy storage devices utilizing PPy/nanocellulose electrodes typically exhibit capacitances of 43 F/g (or 6.8 F/cm²) at mass loadings as high as

157 mg/cm^2 [8]. They comprise PPy coated cellulose fibrils (100 nm in di-
 50 ameter) which form a highly porous network (pore sizes in the range from
 51 hundreds of nanometer to a few micrometers) which can be interpenetrated
 52 with electrolyte. Such composites can display a broad variety in morphology,
 53 hydrophilicity, and electronic and ionic conductivities [18–23]. These com-
 54 posites are targeted for use as biocompatible conductors, biosensors, elec-
 55 tromechanical devices, organic electronics, electroresponsive membranes ac-
 56 tuators, etc. [24, 25]. The electrochemical kinetics in such PPy/nanocellulose
 57 energy storage devices (a schematic is shown in Figure 1) is a central issue
 58 for developing useful applications. In this context, it is critical to understand
 59 if the total charge transport is controlled by the diffusivity in the electrolyte
 60 or within the composite electrodes.

61 The electrochemical properties of the PPy/nanocellulose composite have
 62 previously been investigated by for example cyclic voltammetry (CV) and
 63 electrochemical impedance spectroscopy (EIS) [23], but these techniques have
 64 not yet been able to resolve the fundamental questions on the limiting charge
 65 transport in processes during electrochemical redox conversion. Electrochem-
 66 ical impedance spectroscopy (EIS) is a standard technique for studying dif-
 67 fusion in complex materials in combination with equivalent circuit methods
 68 (ECM), where each circuit element represents a physical phenomenon. How-
 69 ever, this simplified representation may cause misunderstandings of the ex-
 70 perimental data if not used carefully: several equivalent circuits can follow
 71 the same function of frequency but with different corresponding elements,
 72 and a successful fit can often be achieved simply by using a large num-
 73 ber of parameters. For a meaningful parametrization, an a priori model is
 74 necessary [26]. Significant efforts to describe anomalous impedance for finite
 75 systems have been made by for example Bisquert et al. [27] and Macdon-
 76 ald et al. [28–30]. Analytical solutions by White et al for porous electrodes
 77 and insertion systems [31, 32] offer insights into the impedance of such sys-
 78 tem. Here, we apply a similar approach using a ‘multiphysics’ model by
 79 addressing electrochemical impedance as a response of various interfacial
 80 (macroscopic electrode/electrolyte, interfibril diffusion) and interphase (ion
 81 insertion, trapping of ions, resistance, conductivity) properties and processes.
 82 In general, the electrochemical charge and discharge processes in a porous
 83 morphology can be viewed as a propagating boundary between the insulat-
 84 ing (discharged) and conducting (charged) phases. This boundary is associ-
 85 ated with the percolating conducting paths in the polymer composite with
 86 various diffusion lengths, and thus determines the overall impedance spec-

tra. [26] In this present study, a one-dimensional and isothermal model of the PPy/nanocellulose based energy storage device is developed in order to predict impedance spectra which are highly dependent on charge transport properties. The simulated EIS spectra are then compared to experimental results, aiming at resolving the fundamental diffusivity properties in the devices. The evolution of the current signal and its dependence on diffusion, porosity and mass transfer has been modelled. The ionic diffusion in the electrolyte has been systematically altered by varying the sucrose content between 0 and 50 wt% in the 1M NaCl electrolyte solution, following the approach by Aoki et al. [24, 25].

Figure 1: Schematic of the PPy/nanocellulose energy storage device.

2. Experimental

2.1. Material synthesis and electrode construction

Cellulose from the *Cladophora* sp. algae was extracted as described previously [15]. Pyrrole, iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium chloride

101 (NaCl), hydrochloric acid (HCl (aq)), Tween-80, and sucrose were purchased
102 and used as received from Sigma-Aldrich. Deionized water was used through-
103 out the synthesis.

104 300 mg of cellulose were dispersed in 60 mL water using a Sonics VibraCell
105 sonicator. A solution of 1.5 mL of pyrrole and one drop of Tween-80 in 50
106 mL 0.5 M hydrochloric acid was added to the cellulose dispersion and the
107 mixture was stirred for 5 minutes. Polymerization was initiated by addition
108 of a solution of 12.86 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 mL of 0.5 M HCl (aq), and the
109 polymerization was left to proceed for 30 minutes. The resulting black slurry
110 was transferred to a Büchner funnel and was washed with 5 L of 0.5 M
111 HCl (aq) followed by 1 L of 0.1 M NaCl solution. Finally, the water was
112 drained from the funnel, and the remaining filtrate was pressed and dried in
113 an heat press at 70° C for 15 minutes, after which it was left to dry at room
114 temperature to yield a black, paper-like material.

115 2.2. Cell assembly

116 Symmetric energy storage two electrode cells were assembled contain-
117 ing two 45 ± 10 mg, 1×1 cm² sized pieces of PPy/cellulose as electrodes,
118 separated by a 50 μm thick cellulose paper (TF40, Nippon Kodoshi). The
119 electrodes were contacted using rectangular 1.5×5.0 cm graphite foils with
120 a thickness of 0.015 cm (Sigraflex F01513 Z). Electrolyte comprising 2 M
121 NaCl aqueous solutions with addition of 0, 40 or 50 wt% of sucrose purged
122 in nitrogen, respectively. The cells were hermetically sealed in laminated
123 aluminum pouches by heat pressing with the current collectors sticking out
124 of the cell. During electrochemical testing, the cells were pressed between
125 plastic plates using a paper clip.

126 2.3. Electrochemical measurements

127 EIS measurements were performed with a CH Instruments 660D poten-
128 tiostat at OCP on symmetric two electrode cells. The applied ac potential
129 had an amplitude of 5 mV and a frequency varying between 82.5 kHz and
130 0.01 Hz.

131 A three-electrode setup was constructed for CV utilizing a coiled Pt wire
132 as counter electrode and a Ag/AgCl reference electrode with 2 M NaCl (aq)
133 purged in nitrogen. The PPy/cellulose composite sample was mounted on
134 a Pt wire and employed as working electrode. Cyclic voltammetry (CV),
135 galvanostatic charge and discharge measurements were performed with an
136 Autolab PGSTAT302 N potentiostat. CV measurements were conducted

137 at a scan rate of 5 mV/s between 0.4 V and -0.8 V vs. Ag/AgCl, and
 138 galvanostatic charge and discharge experiments were carried out using an
 139 applied current of 1 mA for the same voltage window.

140 CV measurements of the symmetric two electrode cell were conducted at
 141 a scan rate of 5 mV/s between 0 V and 0.8 V cell potential.

142 2.4. Scanning Electron Microscopy (SEM)

143 Surface micrographs were recorded with a LEO1550 field emission SEM
 144 instrument (Zeiss) employing in-lens secondary electron detector. The sam-
 145 ples were mounted on Al stubs with double-sided adhesive carbon tape.

146 3. Finite Element Studies:Model Design

147 The fundamental electrochemical description used in ECM modelling of
 148 energy storage devices is straightforward (Eqs 1-6). For a single step charge
 149 transfer process, $O + ne^- \rightleftharpoons R$, the current voltage are related has

$$\frac{i}{i_0} = \frac{\delta C_O}{C_O^0} e^{\alpha f \eta} - \frac{\delta C_R}{C_R^0} e^{-(1-\alpha)f \eta} + e^{\alpha f \eta} - e^{-(1-\alpha)f \eta} \quad (1)$$

150 where η is overpotential given by $E_{app} - E_{eq}$, $f = F/RT$, i_0 is the exchange
 151 current density, α is transfer coefficient and other symbols have the usual
 152 meaning[13]. Linearising for small η , we get

$$i = i_0 \frac{RT}{nF\eta} \quad (2)$$

153 The total impedance ($Z(\omega)$) can be written as,

$$Z(\omega) = R_{ct} + \sigma/\omega^{1/2} + 1/Q\omega^\beta + 1/\omega C_{dl} \quad (3)$$

154 where R_{ct} is the charge transfer resistance, C_{dl} is the double layer capacitance,
 155 Q is the CPE and σ is the Warburg coefficient as given below:

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2D}} \left(\frac{1}{C_O^0} + \frac{1}{C_R^0} \right) \quad (4)$$

156 However, this set of equations fails to provide a complete description of com-
 157 plex electrochemical system, such as those comprising conducting polymers.
 158 This is generally due to the porous morphology not taken into account, and

Table 1: Energy storage device impedance parameters and limitations

Frequency	10 Hz-1mHz
Current-amplitude	± 10 mA
Not taken into account	Temperature, swelling of film, volume changes, shifting doping levels

therefore transport dynamics is not resolved, but rather embedded into the CPE element which in this context provides a too crude description. Instead, numerical modeling using domain-wise physics and a mathematical description which addresses the hierarchy of process at different length and time scales are needed to capture the details of the transport processes in these systems.

3.1. Model Background

In porous electrodes, the measured impedance is the cumulative signal of spatially distributed processes involving the variation of electrical currents and electrochemical potential throughout the porous layer [33]. The symmetric PPy/cellulose based energy storage devices contain two electrodes with electrical potentials related to the redox processes of polypyrrole, and an electrolyte of aqueous salt solution. In this context, we have excluded phenomena such as film swelling, volume changes and shifting doping levels (pointed out in Table 1). The relevant electrochemical processes can be then distinguished as:

- i) Electronic current conduction in and among the fibers of the electrodes.
- ii) Mass transport in the electrolyte, introducing concentration overpotentials. Here, this is obtained from experimental data.
- iii) Mass transport among the electrode fibers .
- iv) Butler-Volmer electrode kinetics

Fig 1 shows a schematic of the modelled symmetric PPy/nanocellulose composite energy storage device, with the various domains and length scales at cell and electrode level highlighted. Ds_{pos} (or the corresponding Ds_{neg}) denotes the ionic diffusion in the electrodes, while D_l denotes the diffusion in the electrolyte.

185 3.2. Boundary conditions

186 The model comprises a cell cross section in one dimension, implying that
 187 edge effects in length and height are neglected. The cell is constituted in three
 188 regions (two electrodes and a separator) that imply four distinct boundaries
 189 at:

- 190 a) $x = 0$: Negative current collector
- 191 b) $x = \delta_n$: Negative porous electrode/Separator interface: $100 \mu m$
- 192 c) $x = \delta_s$: Separator/Positive porous electrode: $52 \mu m$
- 193 d) $x = \delta_p$: Positive current collector $100 \mu m$

194 For the electronic current balance, a potential of 0 V is set on the counter
 195 electrodes current collector($x = 0$) boundary. At the working electrode cur-
 196 rent collector/feeder ($x = \delta_p$), the current density (harmonic perturbation) is
 197 specified. The inner boundaries facing the separator ($x = \delta_n$ & δ_s) are insu-
 198 lating for electric currents. For the ionic charge balance in the electrolyte, the
 199 current collector boundaries ($x = 0$ & δ_p) are ionically insulating. Insulating
 200 conditions also apply to the material balances.

201 3.3. Electrochemical description

202 The two electrodes are assumed electrochemically porous. Regions 1($0 <$
 203 $x < \delta_n$) and 3 ($\delta_s < x < \delta_p$) therefore contain both solid (PPy/cellulose)
 204 and liquid (electrolyte) phases (see Fig 1). At the particle surface in the
 205 model, the material flux is determined by local electrochemical reaction rate
 206 given by linearized Butler-Volmer kinetics. The electrical potential in the
 207 electron conducting phase, ϕ_s , is calculated using a charge balance based
 208 on Ohm's law where the charge transfer reactions result in a mathematical
 209 source or sink term. Taking porosity and tortuosity into account, the effective
 210 conductivities of the electrodes (ϕ_{eff}) is given by:

$$\phi_{eff} = \phi_0 \epsilon^\gamma \quad (5)$$

211 where γ is the Bruggeman coefficient, set to 1.5 in this model, and ϕ_0 is
 212 the conductivity of the material corresponding to a packed bed of cylindrical
 213 particles, representing the fibrils. The ionic charge balances and material
 214 balances are modeled according to the equations 10 - 12 for binary 1:1 elec-
 215 trolytes. Fickian diffusion describes the mass transport of chloride counter

ions to the particles (eq. 6), whereby the resulting diffusion equation can be expressed for the concentration gradients of counter ions in the composite (eq. 7). Butler-Volmer electrode kinetics describes the local charge transfer current density in the electrodes and are introduced as source or sink terms in the charge balances and material balances (eq. 10- 12).

Counter ion diffusion of the spherical particle of radius r , is described by the Fick's law according to previous work [34, 35]:

$$\frac{\partial}{\partial t} \delta C_i = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right) \quad (6)$$

The counter ion concentration is monitored by

$$\frac{\partial(\epsilon_e C_i)}{\partial t} = \frac{\partial}{\partial x} \left(D_I \frac{\partial C_i}{\partial x} \right) + \frac{1 - t_l^0}{F} j \quad (7)$$

with

$$\left. \frac{\partial C_i}{\partial x} \right|_{x=0} = \left. \frac{\partial C_i}{\partial x} \right|_{x=L} = 0 \quad (8)$$

Charge conservation in the solid phase of each electrode is defined by the Ohms law:

$$\frac{\partial}{\partial x} \left(\sigma^{eff} \frac{\partial \phi_s}{\partial x} \right) - j = 0 \quad (9)$$

with the following limit conditions at the current collectors

$$\sigma_-^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=0} = \sigma_+^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=L} = \frac{I}{A} \quad (10)$$

and the null current conditions at the separator:

$$\left. \frac{\partial \phi_s}{\partial x} \right|_{x=\delta_n} = \left. \frac{\partial \phi_s}{\partial x} \right|_{x=\delta_n+\delta_s} = 0 \quad (11)$$

If $\phi_i(x, t)$ denotes the electrolyte potential, charge conservation in the electrolyte is defined by:

$$\frac{\partial}{\partial x} \left(\kappa^{eff} \frac{\partial \phi_i}{\partial x} \right) + \frac{\partial}{\partial x} \left(\kappa_D^{eff} \frac{\partial}{\partial x} \ln(C_i) \right) + j = 0 \quad (12)$$

231 with

$$\left. \frac{\partial \phi_i}{\partial x} \right|_{x=0} = \left. \frac{\partial \phi_i}{\partial x} \right|_{x=L} = 0 \quad (13)$$

232 where κ^{eff} is the conductivity in the electrolyte. The four differential equa-
233 tions 6,7,9,12 are linked by the Butler-Volmer equation

$$j = a_s i_0 \left(e^{\frac{\alpha n F \eta}{RT}} - e^{\frac{(1-\alpha) n F \eta}{RT}} \right) \quad (14)$$

234 In equation 14, j is induced by overvoltage η , defined by the potential differ-
235 ence between the solid phase and the electrolyte and equilibrium thermody-
236 namic potential U :

$$\eta = \phi_s + \phi_i - U \quad (15)$$

237 where U is a function of the solid phase concentration at the particles. The
238 final impedance response of the device is then generated through the diffusive
239 flux of the charges species.

240 3.4. Material Properties

241 The material properties used in the simulations are as closely as possi-
242 ble mimicking those of a typical PPy/nanocellulose composite. The elec-
243 trolyte is 1 M NaCl in 0%, 40% and 50% sucrose solutions, while the elec-
244 trode materials are PPy/cellulose composites for both negative and posi-
245 tive electrodes. The electrolyte conductivity and the equilibrium potential
246 of the electrodes used have been reported in the literature and previous
247 studies[7, 8, 10]experimentally determined. The volume fraction occupied
248 by the electrolyte inside the porous composite electrode has been accounted
249 for in the model. A complete set of the parameters used can be found in
250 Table 2.

251 3.5. Mesh density and solver settings

252 Eqs 6-15 have been solved using the COMSOL Multiphysics 4.1 software.
253 A mesh length of 3.35×10^{-4} m was used, and the device divided into 47
254 mesh elements in total using 4 vertex elements. The element length ratio
255 has an average mesh growth rate of 1.083. The same mesh was used in all
256 simulations. PARallel DIrect SOLver (PARDISO) is a robust solver for large
257 sparse symmetric or structurally symmetric linear systems of equations on
258 shared memory multiprocessors. Here it is used for fast convergence of the
259 time dependent solution. A PARDISO solver with 0.01 relative and 0.001
260 absolute tolerances was used for the time dependent matrix equations.

261 4. Result & Discussion

262 4.1. Electrode Morphology

263 Fig 2 shows the SEM images of the prepared PPy/cellulose composite
 264 electrodes at high and low resolution. As can be seen, the obtained composite
 265 is made up from randomly oriented fibres in good agreement with previous
 266 results [8]. The PPy/cellulose fibers have an average diameter of ca. 100 nm,
 267 with a homogeneous coating of PPy on the Cladophora cellulose [15]. The
 268 entangled microfibers create voids with pore sizes of hundreds of nanometers
 269 to micron size within the composite.

Figure 2: Low (a) and high (b) magnification SEM images of synthesized polypyrrole/cellulose composite electrodes.

270 4.2. Galvanostatic cycling

271 A galvanostatic charge/discharge curve of the PPy/cellulose composite
 272 with an applied current of ± 1 mA in a potential range of -0.8 and 0.4 V vs
 273 Ag/AgCl is shown in Fig 3. The specific capacitances, C_{sp} , for the charge

274 and discharge of the sample were calculated to 130 and 182 F/g, respectively,
 275 according to:

$$C = \frac{i}{m \frac{dE}{dt}} \quad (16)$$

276 Where i denotes the applied current, m_{tot} denotes the mass of the sample
 277 of 7.1 mg, and dE/dt is the slope of the linear fit to the discharge and
 278 charge curve between -0.4 V and 0.4 V vs. Ag/AgCl, respectively. The
 279 corresponding cell capacitance C_{cell} for a symmetric device was calculated to
 280 38 F/g according to :

$$C_{cell} = \frac{1}{2m_{tot}(\frac{1}{C_{sp}^{pos}} + \frac{1}{C_{sp}^{neg}})} \quad (17)$$

281 where C_{sp}^{pos} and C_{sp}^{neg} denotes the specific capacitances obtained from the
 282 galvanostatic charge and discharge curves, respectively. As can be seen in
 283 Fig 3 , the results show the symmetric charge storage device, which is a
 284 maintained as such in the model implemented.

285 4.3. Cyclic Voltammetry

286 Fig. 4a and b presents CV data for two- and three-electrode setups, re-
 287 spectively, displaying characteristic electrochemical response of PPy. In Fig.
 288 4a, the rectangular shape of the voltammogram indicates a supercapacitor re-
 289 sponse for the two electrode cell configuration. The capacitance is calculated
 290 to be 35 F/g from these measurements using:

$$C_{cell} = \frac{\Delta Q}{m_{total}} \Delta E \int \frac{i dt}{dE} \quad (18)$$

291 In Fig. 4b, characteristic PPy oxidation and reduction voltammetric re-
 292 sponses are observed, with an oxidation onset at -0.4 V and hysteresis upon
 293 scan reversal giving a full reduction at -0.7 V, for all different sucrose con-
 294 centrations. It is evident that the voltammetric response differs from the
 295 ideal double-layer capacitive response since the voltammograms features clear
 296 peaks in the oxidation and reduction voltammetric responses. The CV re-
 297 sults demonstrate that the charge storage for these composite electrodes is
 298 primarily based on the oxidation and reduction of the PPy coatings present
 299 on the cellulose matrix. The oxidation and reduction charges obtained from
 300 the voltammograms correspond to 22 C g⁻¹ in the potential range between
 301 -0.447 V and 0.4 V vs. Ag/AgCl, which translates to a specific electrode

302 capacitance of 145 F g^{-1} and a cell capacitance of 36 F g^{-1} assuming a
 303 symmetric charge storage device, which is comparable with the capacitances
 304 obtained from galvanostatic charge and discharge measurements. Carlsson
 305 et al. [36] observed that porosity of the samples affected the shape and size
 306 of the voltammograms. They attributed this to the counter ion diffusion and
 307 mass transport inside the composite and in the vicinity of the fibers. In their
 308 results, the shape of the oxidation peak is strongly influenced by the mass
 309 transport of counter-ions and their access to the PPy layer. Here, a similar
 310 effect was implemented through changing the diffusion coefficient of the ions
 311 by the electrolyte viscosity. This, in turn, slows down the evolution of the
 312 diffusion length ($\sqrt{D_l/\omega}$). It can be seen that the PPy oxidation peaks are
 313 shifted to more positive potentials with increasing viscosity while the reduc-
 314 tion peaks become broader and less distinct. This dependence of the shape
 315 of the voltammograms is in accordance with the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta R} \quad (19)$$

316 where D is the diffusion coefficient, R is the radii of diffusing ion and η is the
 317 viscosity of the solvent. Using tabulated values for η , the diffusion coefficients
 318 for the chloride ions can be estimated to $1.0 \times 10^{-9} \text{ m}^2/\text{s}$, $2.2 \times 10^{-12} \text{ m}^2/\text{s}$ and
 319 $1.1 \times 10^{-12} \text{ m}^2/\text{s}$ for 0, 40 and 50% sucrose content, respectively. Moreover,
 320 the CV results demonstrate that solely the diffusion coefficient is affected by
 321 the addition of sucrose, and does not give rise to any other electrochemical
 322 process.

Figure 3: Galvanostatic charge and discharge curves of a symmetric PPy/nanocellulose supercapacitor device in 2 M NaCl in a three electrode set-up with Pt-wire as counter electrode and Ag/AgCl reference.

4.4. Impedance spectroscopy

Figure 5 shows the Nyquist plots depicting the ac impedance response of a selection of the PPy/cellulose cells in 0 wt%, 40 wt% and 50 wt% of sucrose solution. The as-synthesized PPy/cellulose composite has an OCV of 0.3 V vs. Ag/AgCl, thus, both electrodes in a symmetric PPy/cellulose cell will initially be at 0.3 V Ag/AgCl. The spectrum for 20% sucrose overlapped with 40% sucrose solution and was hence less useful, while solutions with >50% were not used due to that the amount of sucrose then approaches the dissolution limit. (Table 3 summarises the parameters used for the simulation) . All cells were found to give a response similar to that expected for a classical Randles equivalent circuit [37] containing: (i) a resistance element (determined from the high frequency intersect with the real axis of the Nyquist plots) in series with (ii) a circuit containing a charge transfer resistance; (iii) a diffusion element of finite-length Warburg type [37, 38] originating from diffusion of counter ions in the electrode material; and (iv) a double layer

Figure 4: Cyclic voltammogramsetry curves at 5 mV/s of (a) a symmetric two electrode cell utilizing PPy/cellulose composite in 2 M NaCl and (b) PPy/cellulose in 2 M NaCl with varying addition of sucrose (0, 20, 40, and 50 wt-%) in a three electrode assembly set-up with PPy/cellulose Pt-wire as counter electrode with and a Ag/AgCl reference.

capacitance (connected in parallel with (ii) and (iii)), represented by a constant phase element (CPE). The finite-Warburg diffusion element dominates the response in the low frequency region of the Nyquist plots, in which the counter ions diffusing into the electroactive PPy layer become blocked by the current collector. The vertical line in this region is indicative of a capacitive behavior, which is explained by finite-Warburg diffusion which will be seen at sufficiently low frequencies. The absence of a semicircle in the Nyquist plots further indicates that the electrochemical behavior of the electrodes is unaffected by electron transfer limitations, in good agreement with previous findings [39]. When going from low to higher frequencies, a diffusion-controlled region can be seen as a sloping line. The experimental EIS data in figure 5 are in good agreement with the simulated impedance results. This means that the electrochemical reactions within the materials of the present energy storage unit mainly involve oxidation and reduction of the PPy layer along with charging of the double layer. The material is assumed to be porous enough to allow the PPy layer to be rapidly oxidized and reduced through-

Figure 5: Comparison of the experimental data with simulation curves. The solid lines are simulated curves and the dotted lines are experimental data. Inset curves show the scaled images for clarity of the fit.

out the matrix, meaning that there should be a sufficiently high amount of electrolyte within the electrodes. Furthermore, the good agreement between the simulated impedance response and the experimental EIS data is a strong validation of the model used.

It can be assumed that the rate constant for charge consumption complies with the Butler-Volmer equation and that the potential varies linearly in response to the consumed charge on PPy during the Faradaic process[35]. In this context, it is important to note that since the geometry of the fibrous cellulose does not conform to the model of a homogeneous slab, the diffusivity in the composite electrode can only be interpreted as an overall integrated average (i.e., a macroscopic diffusion coefficient $D_{s_{pos}}$), also including the

Figure 6: Nyquist plot showing the diffusion of counter ions in an electrolytic solution in response to diffusion in the PPy/cellulose composite. The diffusion coefficient in the porous composite geometry is $Ds_{pos} = Ds_{neg} = 5 \times 10^{-10} m^2/s$. Other parameters are as in Table 2. Inset curves show the scaled images for intermediate frequency region.

liquid phase filling the available space between the polymer fibrils. At room temperature and ambient atmospheric pressure, however, it is uncertain how much liquid actually enters the 50 nm diameter fibrils, and it is therefore impossible to distinguish between the transport along the fibrils, or between them in the electrolyte phase. To understand the transport limitations better, we have therefore here varied the diffusion coefficient in the model for three different situations (where Ds_{pos} is diffusion coefficient inside the positive electrodes and D_l is the diffusion coefficient between the electrodes): $Ds_{pos} < D_l$, $Ds_{pos} \approx D_l$ and $Ds_{pos} > D_l$.

374 The resulting impedance data from these three situations are summarized
 375 in Nyquist plots in figure 6. The different situations can capture the onset
 376 for the two diffusion processes, one within the composite electrode material
 377 and one within the electrolyte. It has been observed in previous studies[36]
 378 that the amount of chloride ions present in the porous samples influences the
 379 rate of redox conversion.

380 This observation, along with the present results, implies that a large num-
 381 ber of counter ions would have to diffuse from the bulk electrolyte solution
 382 outside the composite and through the composite pore network to reach all
 383 PPy coated fibers during the oxidation process. This means that:

384 (i) If the diffusion coefficient inside the electrode matrix $D_{s_{pos}}$ is smaller
 385 than the diffusion coefficient in the electrolyte D_l ($D_{s_{pos}} < D_l$) correspond-
 386 ing to the situation when no sucrose is added, then the counter ion diffusion
 387 primarily yields a pseudocapacitive response with a short Warburg arm rep-
 388 resenting diffusion in the liquid phase followed by counter ion accumulation
 389 on the fibril or composite. (ii) If $D_{s_{pos}} \sim D_l$ a pseudo kinetic barrier ap-
 390 pear and yield a corresponding impedance response. As seen from the model
 391 implemented, this response is due to an interplay of diffusion, morphology,
 392 porosity and volume fractions occupied by each phase. (iii) If $D_{s_{pos}} > D_l$, the
 393 counter ion diffusion will be slower in the electrolyte than in the electrode,
 394 and therefore dominate the impedance response. The charge compensation
 395 process then mainly involves diffusion of chloride ions present in the compos-
 396 ite fibers.

397 The excellent agreement between simulated response and experimental
 398 data, shown in figure 5, suggest that the addition of sucrose only affects
 399 the diffusion coefficient in the electrolyte, as a variation in D_l is sufficient
 400 to fully account for the impedance response using different sucrose contents.
 401 Furthermore, the onset frequency for finite length diffusion varies with su-
 402 crose content; 0.83 Hz for 0 wt-%, 0.056 Hz for 40 wt-%, and 0.026 Hz for
 403 50 wt-%. This clearly marks a dependence of the onset frequency on the
 404 diffusion properties of the counter ion. With the present result at hand the
 405 "finite length diffusion response (vertical line)" observed at low frequencies
 406 must be interpreted as an interplay between counter ion diffusion within the
 407 electrolyte-filled pores of the flooded PPy/cellulose composite and counter
 408 ion diffusion in the electrolyte. This could very well be related to the charg-
 409 ing time of the device as a whole or the average time required for the counter
 410 ion to diffuse and get consumed at electroactive fibrils. Furthermore, since
 411 the onset frequency for finite length diffusion is related to the diffusion co-

efficient of the counter ion in the electrolyte, it can be concluded that there is a close relation between pore structure and impedance response. These results would have predicted an independence of onset frequency for finite length diffusion with respect to composite electrode thicknesses (above 36.4 to 6.3 μm)(refer table 3), as previously observed [8]. In this previous study, it was concluded that the frequency for the onset of finite length diffusion was independent of the separator and composite thickness, and ascribed the large amount of electrolyte containing pores to render similar diffusion behavior, irrespective of electrode thickness. It indicates the role of the intermediate length scales present in the composite structure possibly due to the porous network or mesostructure of these composites which yield a blocking effect or the pseudocapacitance of the system. This further indicates that for systems which have sluggish diffusion kinetics like ionic liquids can be used to tune in the response time of the assembly.

5. Conclusions

In the present work, Finite Element Methodology has been used to model the impedance response of a symmetric PPy/cellulose composite energy storage device. A model has been constructed which can offer insight into the diffusion inside the porous composite and the diffusion between the positive and negative electrodes. The EIS data is simulated without using the conventional equivalent circuit analysis; instead the model uses fundamental electrochemical descriptions of both Faradaic and non-Faradaic processes inside the cell. Along with experimental data, it has been demonstrated that the charge transport in the electrodes is mainly controlled by the diffusion of counter ions in the electrolyte within the matrix. The onset frequency for pseudocapacitive response in the cell assembly is found to be dependent on the sluggish diffusion kinetics in the PPy/cellulose composites. Of the two diffusion processes of counter ions inside the cell, i.e. in the bulk electrolyte and inside the flooded composite, the slower process controls the gradient of the counter ions and hence the impedance response. The effect of limiting the diffusion coefficient of chloride counter ions in the electrolyte helps resolving the transport processes between the electrodes and among PPy/cellulose fibrils. The expanded understanding of the ion transport within these cells will be essential to improve the response time of the energy storage device.

Table 2: List of Symbols & Parameters

Variable	Value [SI Units]	Description
Ds_{neg}	$7.5 \times 10^{-14}[m^2/s]$	Diffusivity in Negative Composite Electrode
Ds_{pos}	$7.5 \times 10^{-14}[m^2/s]$	Diffusivity in Positive Composite Electrode
rp_{neg}	$100 \times 10^{-7}[m]$	Particle radius Negative
rp_{pos}	$100 \times 10^{-7}[m]$	Particle radius Positive
T	$298[K]$	Temperature
t_l	0.363	Counter ion transport number
D_l	$7.5 \times 10^{-12}[m^2/s]$	Salt diffusivity in Electrolyte
Ks_{pos}	$574.8[S/m]$	Solid phase conductivity Positive
Ks_{neg}	$574[S/m]$	Solid phase conductivity Negative
cl_0	$2000[mol/m^3]$	Initial electrolyte salt concentration
$csmax_{neg}$	$25134[mol/m^3]$	Max solid phase concentration Negative
$csmax_{pos}$	$25134[mol/m^3]$	Max solid phase concentration Positive
k_{neg}	$20 \times 10^{-8}[m/s]$	Reaction rate coefficient Negative
k_{pos}	$2 \times 10^{-8}[m/s]$	Reaction rate coefficient Positive
L_{neg}	$100 \times 10^{-6}[m]$	Length of negative electrode
L_{sep}	$52 \times 10^{-6}[m]$	Length of separator
L_{pos}	$100 \times 10^{-6}[m]$	Length of positive electrode
i_{pert}	$10[mA/cm^2]$	Perturbation Current

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Table 3: Parameters used in simulations

Parameters	0%	40%	50%
Viscosity($N.s/m^2$)	0.001	0.3	0.6
$D_l(m^2/s)$	1.1×10^{-9}	2.2×10^{-12}	1.1×10^{-12}
$Ds_{neg}(m^2/s)$	7.5×10^{-14}	7.5×10^{-14}	7.5×10^{-14}
$Ds_{pos}(m^2/s)$	7.5×10^{-14}	7.5×10^{-14}	7.5×10^{-14}
$K_{neg}(m/s)$	2×10^{-8}	2×10^{-8}	2×10^{-8}
$K_{pos}(m/s)$	2×10^{-8}	2×10^{-8}	2×10^{-8}
Conductivity(S/m)	574	574	574
Ionic radii nm (Hydrated Chloride)	0.33	0.33	0.33
Onset Frequency(Hz)	0.83	0.056	0.026
Diffusion layer thickness($\sqrt{D_l/\omega}$)(μm)	36.4	6.5	6.3

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