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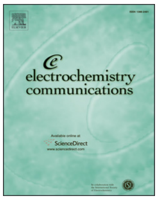

Self-discharge in positively charged polypyrrole–cellulose composite electrodes

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ABSTRACT

Self-discharge is one of the most critical issues to address to allow for industrialization of conducting polymer (CP) based electric energy storage devices. The present work investigates the underlying cause of self-discharge in positively charged polypyrrole (PPy), which is one of the most frequently studied CPs for such devices. The analyzed material is a composite of PPy and cellulose from *Cladophora* sp. algae forming a free standing paper-like material. From the time dependence of the potential decay as well as from independent spectroelectrochemical investigations the decay was attributed to a kinetically limiting Faradaic reaction, intrinsic to the polymer, forming a reactive intermediate that irreversibly reacts with its surroundings in a kinetically non-limiting following reaction. As such, nucleophilic addition of electrolyte nucleophiles is not found to be rate-determining. These results provide insight into the self-discharge phenomenon in p-doped CPs, and information regarding the potential range in which CPs can operate with insignificant self-discharge.

1. Introduction

Conducting polymers (CPs) are interesting for creating organic electrical energy storage devices with a smaller carbon footprint compared to traditional contemporary batteries [1–5]. The intrinsic conductivity and redox properties of CPs open up for two different approaches to electrical energy storage. One way is to utilize the pseudocapacitance of the CPs, which implies high doping levels to reach competitive specific capacities [6–9]. Another way, that has recently gained impetus, is to introduce high capacity redox active functional groups as capacity carrying component and to utilize the CPs to render the material conducting [2,10–14]. Irrespective of strategy, knowledge of the potential limits is instrumental for adopting design strategies in the development of such electrical energy storage devices.

A well-documented issue with CPs is their rapid self-discharge, i.e. potential drop towards the uncharged state. We have previously investigated the self-discharged seen in symmetrical cells with polypyrrole (PPy)/cellulose composite electrodes [15]. The self-discharge rate was found to be independent of electrode size, electrolyte and salt used in the synthesis of PPy. Furthermore, lowering the pH of the aqueous electrolyte had no significant effect on the self-discharge rate. It was found that the self-discharge of the negative electrode was due to residual oxygen in the electrolyte, while the self-discharge of the positive electrode was due to an activation controlled Faradaic reaction. A degradation product, maleimide, was found in the cells after self-discharge.

The present work aims at further investigating the underlying cause of self-discharge of positively charged PPy. To this end we evaluate the potential loss during open circuit conditions in a three-electrode setup with the above-mentioned PPy/cellulose composites as working electrode. We also show new spectroscopic results regarding maleimide formation during potential hold experiments with the composite.

2. Experimental

PPy composites were prepared with *Cladophora* sp. algae cellulose [16]. A pyrrole solution (50 ml 0.43 M in 0.5 M HCl) was mixed with a dispersion of cellulose (300 mg to 60 mL water) and 100 ml 0.48 M $FeCl_3$ solution was added. The reaction proceeded for 30 min, after which the composite was washed and dried. The synthesis is described in more detail in a previous paper [15].

Three-electrode measurements were carried out using an Autolab PGSTAT302N potentiostat (Ecochemie, the Netherlands). A coiled Pt wire was used as counter electrode (kept in a separate compartment) and a 3 M NaCl Ag/AgCl as reference electrode (all potentials are given against Ag/AgCl i.e. 0.192 V vs. NHE [10]). The electrolyte was purged with nitrogen and was kept under nitrogen blanket throughout all experiments. Self-discharge of PPy was measured by charging the composite with a potential step to 0.53 V during 600 s followed by monitoring of the potential decay at open circuit. During the potential step charging, the current dropped down to a constant low value. Another measurement was also carried out where a constant voltage was applied to the sample and the leakage current was measured over time while carefully stirring the electrolyte (50 ml). During these

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measurements the electrolyte pH as well as the spectral evolution of the electrolyte solution was measured. The pH was measured using a Metrohm 744 pH meter and the spectral evolution monitored using an UV-1800 spectrophotometer (Shimadzu, Japan).

3. Results

A full characterization of the composite material has been carried out previously [17,18] and this paper will be solely dedicated to investigating the self-discharge characteristics of positively charged PPy. The self-discharge of the positive electrode was previously found to be due to an activation controlled Faradaic reaction.[1] The potential decay for such a reaction in a capacitor, such as our composite material, is given by Eq. (1) [15].

$$\Delta E = -\frac{\overline{R}T}{\alpha F}\ln\left(\frac{\alpha F i_0}{\overline{R}TC}\right) - \frac{\overline{R}T}{\alpha F}\ln\left(t + \frac{KC}{i_0}\right), \tag{1}$$

with

$$K = \frac{\overline{R}T}{\alpha F}e^{-\frac{\alpha F}{\overline{R}T}\Delta E_i} \tag{1b}$$

where $\overline{R}$ is the gas constant, T the temperature, F is the Faraday constant and C is the capacitance. The fitted parameters are the symmetry factor, (α), and the apparent exchange current (i_0), t is the time and ΔE_i is the potential at $t = 0$.

Fig. 1 shows the potential decay of PPy composite and a fit to Eq. (1). The cell capacitance was evaluated from the RC time constant obtained from the potential step during charging [19] and $\Delta E_i = E - E_r$ was taken as the potential vs. Ag/AgCl at $t = 0$. The reference potential E_r was thus arbitrarily chosen as the potential for the reference electrode rather than the redox potential for the redox reaction responsible for self-discharge. This was necessary since the redox potential (E^0) for the involved Faradaic reaction is unknown. As the potential dependence of the rate constant is expected to comply with the Tafel equation this assumption does not affect the potential time decay. The extracted i_0 does, however, not formally correspond to the exchange current for the redox process, but rather the rate constant at E_r. SI units were used for the remaining constants in the equation. From Fig. 1 it is evident that an activation-controlled Faradaic reaction conforms to the experimental data over the entire observed potential decay.

It is known that PPy degrades at high potentials, with the formation of maleimide as a result [15,20,21]. The degradation reaction at elevated potentials was further investigated by holding a composite at fixed potentials above 0.4 V. A release of maleimide over time could be measured (in the UV–visible region) and the released amount was calculated from standard curves, using the characteristic absorbance peaks at 216 nm and 277 nm. The molar absorptivity ε was found to be 17,271.6 M^{-1} cm^{-1} and 560.1 M^{-1} cm^{-1} for the peaks at 216 nm and 277 nm, respectively. During the potential hold experiments, pH was also logged continually using a pH-meter and the current from the electrochemical measurement was integrated to give the total electric charge. The charge leakage from the measurements mentioned above is shown in Fig. 2a. The simultaneous proton release, calculated from a measured pH change, and the maleimide release are shown in Fig. 2b and c respectively. Finally, spectral evolution for the hold step at 0.6 V is shown in Fig. 2d.

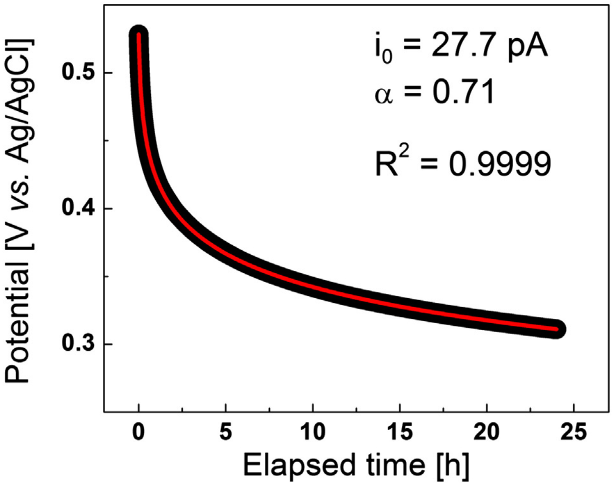

Fig. 1. Self-discharge of a PPy composite (Black line) together with the fit to an activation-controlled Faradaic reaction (Red line). The resulting fit parameters i_0 and α in Eq. (1) are also included (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

4. Discussion

It is well-known that PPy can degrade to form maleimide as a byproduct if the polymer is subjected to sufficiently high potentials [20,21]. From the potential hold experiments (Fig. 2c) it is evident that maleimide is formed already at 0.4 V. At this potential a measureable leakage current as well as a concomitant release of protons is also observed. Both leakage current and proton release increase with a factor of ~10 when a potential step is set to 0.8 V, indicating Faradaic reactions. A similar behavior, for potential steps, has previously been seen by Mazeikiene et al. [22] for PPy. There is a qualitative agreement between charge leakage, proton liberation and maleimide, as seen in Fig. 2. Quantitatively, however, the release of charge and protons cannot be explained by the degradation of PPy to maleimide alone as this reaction only releases four or two protons per maleimide for a terminal and a non-terminal pyrrole unit, respectively [15]. Also the charge per maleimide ratio (13 electrons per released maleimide) is too high to be explained by degradation to maleimide alone. One plausible explanation for the discrepancy could be a subsequent degradation of maleimide. However, a solution of maleimide showed only small spectral changes or other indications of degradation during 7 days of storage in a 0.1 M $NaCl_{aq}$-solution. In addition to maleimide, other degradation products are likely formed. The less oxidized analogue to maleimide, succinimide as well as CO_2 have both been detected as products of PPy degradation [23]. Neither of these products shows applicable absorptions in the wavelength region covered in the potential hold experiments. A complete degradation of a terminal pyrrole unit to CO_2 would result in liberation of 23 protons and 23 electrons. Such degradation would explain the remaining amount of charge leakage, and proton liberation. Furthermore, assuming that all observed self-discharge stems from a complete degradation to CO_2, ~0.04% of the PPy units are sufficient to explain the charge consumed during a self-discharge. The corresponding number for a complete degradation to maleimide is 0.2%. As relatively minor degradation is required to account for complete discharge of the polymer, the process could easily be misinterpreted as a reversible process [24–26] and thus lead to erroneous measures to resolve or circumvent the problem of self-discharge.

Although the maleimide reaction cannot account for the proton release and the leakage current, the similarity of the time evolution of proton release, charge consumption and maleimide production suggests that these products are formed with a common rate-limiting step and hence a common reaction intermediate. The exact nature of this transition state is unknown but the excellent fit of experimental self-discharge data to the model for an activation-controlled Faradaic

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[1] The activation controlled Faradaic reaction implies that 1) positive charge on PPy is consumed, 2) the rate constant for charge consumption complies with the Tafel equation and 3) the potential varies linearly in response to the consumed charge.