Energy harvesting by neutralization pseudocapacitor obtained from phosphomolybdic acid and poly(3,4-ethylenedioxythiophene)

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ABSTRACT

This study proposes the use of pseudocapacitors obtained from self-assembled materials to harvest energy after complete charge/discharge cycles conducted in electrolytic solutions with different pH values. The negative electrode consisted of phosphomolybdic acid (PMA), poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS), and polyallylamine (PAH), whereas the positive electrode comprised electrosynthesized PEDOT. The ability of these electrodes to harvest energy resulted from the partial change in entropy associated with alterations in the proton concentration after neutralization reactions. Investigation of the potentiodynamic profile of the current density and conduction of electrochemical impedance spectroscopy helped to evaluate the practical reversibility of the proton electroinsertion process and to maximize the energy storage efficiency. The electrochemical quartz crystal microbalance data allowed for proposal of a charge compensation mechanism and for assessment of the proton selectivity of the modified electrodes. On the basis of the charge/discharge curves recorded from pH = 1 to pH = 6, the neutralization pseudocapacitor harvested 30.7 kJ per mol of electroinserted proton during H_2SO_4 solution neutralization, which corresponded to 54.6% of the neutralization enthalpy. Together, these results demonstrated the viable application of this methodology to harvest energy during acid wastewater treatment.

1. Introduction

Energy production is one of the main challenges humanity will have to face toward the end of the 21st century [1]. Population growth, ever-rising energy demand per capita, and emission of greenhouse gases by fossil fuel combustion have called for efforts to increase participation of renewable energy sources in the world energy matrix [1]. Currently, an estimated 19% of the total energy production worldwide comes from renewable resources [2]. To achieve greater participation of these renewable energy sources in the world energy matrix, it is vital to improve the efficiency of solar, wind, geothermal, and biomass energy conversion into electricity, which is the main means of energy consumption.

Another possibility to obtain energy from renewable sources is to explore the energetic potential of salinity gradient and convert it into electrical power [3]. To this end, Pattle has proposed the use of a hydroelectric pile, in which alternated layers of salt and fresh water separated by basic and acidic membranes generate membrane electromotive force [4]. Recently, researchers have introduced electrochemical systems to harvest energy. These systems use an appropriate electrochemical cell that can deliver work in the presence of varying concentrations of the electrolytic solution. La Mantia et al. developed mixing entropy batteries

in which they employed a sodium ion intercalation electrode (consisting of $Na_2Mn_5O_{10}$) and an electrode that selectively interacted with chloride ions (silver electrode) [5]. The first step involved cell charging in a solution with low concentration of the electrolyte, followed by replacement of this solution with a more concentrated one. Next, cell discharge took place, which was followed by exchange of the solution with high concentration of the electrolyte for a solution with low concentration of the same electrolyte. At the end of the full electrochemical cycle, the entropic change associated with NaCl transfer from the concentrated solution to the more diluted solution produced electrical work. In the case of excess seawater, this system harvested an estimated 2.5 kJ per cubic decimeter of river water, to convert it into electrical work [5,6].

Capacitive mixing (CAPIMIX) developed by Broglioli is yet another strategy to obtain renewable energy [7]. In capacitive double layer expansion (CDLE), porous materials store charge upon application of an external voltage [7,8]. Capacitive Donnan potential is another method that uses ion-selective membranes to separate cations and anions without the need to apply an external potential [9].

The aforementioned methodologies could use river water instead of seawater as electrolytic solution in the electrochemical system. Energy harvesting from differences in ion concentration could also be explored during acid wastewater treatment. In this sense, energy harvesting could substantially reduce energy consumption during the treatment of this kind of effluent. This approach would encourage wastewater

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treatment and contribute to sustainable growth in the industrial sector [10]. Our group has recently developed neutralization pseudocapacitors that can harvest energy during treatment of acid industrial wastewater, sewage, and swimming pools, for example. The proton insertion process occurred in acidic solution, whereas proton removal took place in neutral (or slightly acidic) medium. In this case, energy harvesting stemmed from the entropy change associated with varying proton concentrations in the aqueous solution during the neutralization process [11].

Electrodes modified with phosphomolybdic acid (PMA), poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS), and poly(allylamine chloride) (PAH) can accomplish selective proton electroinsertion, which is essential to modify the electrical potential in media with different pH values and ensures harvesting of the entropic energy after complete discharge/charge cycles [11]. Moreover, the high conductivity of protons and polarons in PMA and PEDOT [12–14], respectively, tend to diminish the overpotential that builds up during the discharge/charge processes, to increase the stored energy.

This work has investigated the use of the PMA/PAH/PEDOT electrode in electrolytic H_2SO_4 solution at pH = 1 and in K_2SO_4 solution at pH = 6 (simulating H_2SO_4 solution neutralized with KOH), with a view to employing it as the negative electrode in neutralization pseudocapacitors. The high solubility of PMA in aqueous medium prompted the use of the Layer-by-Layer method (LbL) to assemble the electrode—during the self-assembly, PMA should establish electrostatic interactions with PAH [14–16]. The LbL method also allowed for control of the electrode thickness, which helped to suppress diffusion and ohmic overpotentials and promoted synergistic effects originating from the intimate contact between the components [17–19]. This work also evaluated neutralization capacitors in which electrosynthesized PEDOT was the positive electrode, because this conducting polymer should enable sulfate anion electroinsertion/electrodeinsertion [20].
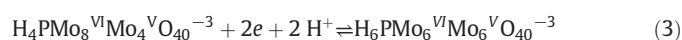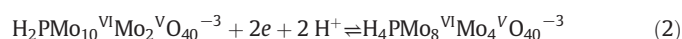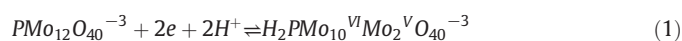
2. Experimental

LbL films were assembled onto a fluor tin oxide (FTO)-coated glass with sheet resistance ≤20 Ω obtained from Flexitec (Curitiba, Brazil). The layers were achieved via ionic attraction of oppositely charged materials, by alternately immersing the FTO substrate in PMA (5 g L^{-1} and pH = 2) and PAH (1.6 g L^{-1} and pH = 2) aqueous dispersions for 1 min. After each layer was deposited, the substrates were rinsed in HCl solution for 30 s (pH = 2). The alternate immersion procedure was repeated 15 times, and the last layer (without immersion of the substrate in the aqueous PAH dispersion) of each LbL film was dried under nitrogen flow. The resulting material will be designated PMA/PAH hereafter. The same procedure was carried out for the assembly of PEDOT/PAH and PMA/PAH/PEDOT LbL films. In the first case, the FTO substrate was immersed in PEDOT-PSS aqueous dispersion (1.3 g L^{-1} and pH = 2), followed by immersion in the PAH (1.6 g L^{-1} and pH = 2) aqueous dispersion. To assemble PMA/PAH/PEDOT LbL films, the FTO substrate was immersed for 1 min in each of the aqueous dispersions, in the following sequence: PMA (5 g L^{-1} and pH = 2), PAH (1.6 g L^{-1} and pH = 2), PEDOT-PSS (1.3 g L^{-1} and pH = 2), and PAH (1.6 g L^{-1} and pH = 2). After deposition of each layer, the substrates were rinsed under the same conditions described above. This immersion sequence was repeated 15 times, and the last layer (without immersion of the substrate in the aqueous PAH dispersion) was also dried under nitrogen flow.

The electrochemical experiments were conducted on an Autolab PGSTAT30 potentiostat/galvanostat. A platinum sheet with an area of 10 cm² and Ag/AgCl in saturated KCl were used as the counter electrode and the reference electrode, respectively. PEDOT was electrosynthesized in an electrolytic solution of KCl at 0.1 mol.L^{-1}. Next, PEDOT was assembled with 3,4-ethylenedioxythiophene (Aldrich, 0.01 mol L^{-1}) on FTO with an area of 1 cm² by performing 30 voltammetric cycles between 0.4 and 1.5 V at 10 mV s^{-1} [21]. To investigate the electrochemical

behavior of the PMA/PAH/PEDOT and PEDOT electrodes, volumes of 20 mL of electrolytic solutions of H_2SO_4 at pH = 1 and of K_2SO_4 at 0.05 mol L^{-1}, pH = 6, were exchanged in a homemade electrochemical cell containing two connections for input and output electrolytic solution, by means of a four-channel peristaltic pump model BT100-1F, acquired from LongerPump. Charge and discharge curves were also performed for a two-electrode electrochemical cell consisting of electrosynthesized PEDOT (positive) and the LbL PMA/PAH/PEDOT (negative) electrodes. The *ac* electrochemical impedance spectroscopy was conducted between 100 kHz and 1 MHz; the *ac* amplitude was 5 mV. For the EQCM experiments, the substrates were placed on 6 MHz AT-cut quartz crystals coated with gold. These crystals had a piezoelectrically and electrochemically active area of 0.361 cm², and an integral sensitivity constant of 0.0815 cm² s^{-1} g^{-1}. The resonance frequency shift was measured with the aid of an HP-5370B Universal Timer/Counter. Changes in the resonance frequency of the EQCM crystal were transformed into mass changes by means of the Sauerbrey equation. Film thickness was analyzed by specular reflectance with the aid of the Nanocalc 2000 program coupled with a single channel 2048 pixel CCD spectrophotometer equipped with halogen lamp as light source. The thickness values measured for the 15-bilayer PMA/PAH, PEDOT/PAH, and PMA/PAH/PEDOT LbL films were 106 ± 4 nm, 120 ± 4 nm, and 108 ± 4 nm, respectively. The geometrical area of the films was 1 cm².

3. Results and discussion

Fig. 1a displays the potentiodynamic profile of the current density (j) recorded for the PMA/PAH, PEDOT/PAH, and PMA/PAH/PEDOT films in H_2SO_4 (pH = 1) at a sweeping rate (ν) of 20 mV s^{-1}. The voltammogram of the PMA/PAH film revealed three redox pairs (Eqs. (1), (2), and (3)), which were associated with the occurrence of electroinsertion/electrodeinsertion reactions during the negative/positive potential scan, respectively. The two-electron and two-proton transfer taking place in the PMA component of the host matrix originated from disproportionation reactions related with odd reduction states I, III, and V [22].

$$PMo_{12}O_{40}^{-3} + 2e + 2H^+ \rightleftharpoons H_2PMo_{10}^{VI}Mo_2^{V}O_{40}^{-3} \qquad (1)$$

$$H_2PMo_{10}^{VI}Mo_2^{V}O_{40}^{-3} + 2e + 2\,H^+ \rightleftharpoons H_4PMo_8^{VI}Mo_4^{V}O_{40}^{-3} \qquad (2)$$

$$H_4PMo_8^{VI}Mo_4^{V}O_{40}^{-3} + 2e + 2\,H^+ \rightleftharpoons H_6PMo_6^{VI}Mo_6^{V}O_{40}^{-3} \qquad (3)$$

On the other hand, the PEDOT-PSS component exhibited broad rectangular voltammetric waves, in agreement with other studies [20,23]. Although the electrochemical response of this component was not explicit in the voltammograms of the PMA/PAH/PEDOT film, PEDOT-PSS helped to increase the charge capacity of the film (9.2 C.cm^{-3}, 6.5 C.cm^{-3}, and 15.2 C.cm^{-3} for the PMA/PAH, PEDOT/PAH, and PMA/PAH/PEDOT films, respectively) at 20 mV s^{-1}. The cyclic voltammograms of the PMA/PAH/PEDOT film also revealed that the proton electroinsertion reactions were only slightly irreversible. The peak potentials remained virtually unaltered as the scan rate changed (Fig. 1b). Additionally, these voltammograms also evidenced a small difference between the peak potentials. At 20 mV s^{-1}, the anodic and cathodic peak potentials (ΔE_p) of the redox pairs I–II, III–IV, and V–VI differed by 13, 14, and 25 mV for the PMA/PAH/PEDOT film, respectively. On the other hand, the redox pairs I–II, III–IV, and V–VI differed by 39, 23, and 37 mV for the PMA/PAH film, respectively.

The low irreversibility of the proton electroinsertion reaction and the highest volumetric charge capacity of the PMA/PAH/PEDOT film were essential to maximize the energy harvested after the full electrochemical cycle during acidic wastewater neutralization. In addition, proton insertion/deinsertion may have taken place to compensate for the electronic charge associated with reduction/oxidation of the