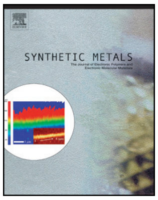
Synthetic Metals 196 (2014) 8–19

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Mn-modified polypyrrole thin films for supercapacitor electrodes

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ARTICLE INFO

Article history:
Received 29 April 2014
Received in revised form 9 July 2014
Accepted 14 July 2014
Available online 2 August 2014

Keywords:
Polypyrrole
Manganese oxides
Supercapacitor electrode materials
Electrochemical quartz crystal microbalance
Atomic force microscopy

ABSTRACT

Thin film Mn-modified polypyrrole (PPy) composite electrodes have been prepared by chronoamperometric electrodeposition and characterized in terms of their physico-chemical and electrochemical properties and performance. Analysis of the chronoamperometric data shows that electrodeposition of the thin film results in a relative increase in electrochemically active surface area of up to 30 times. This finding was supported by transmission electron microscopy (TEM), atomic force microscopy (AFM) and profilometry analysis of the films. Electrochemical quartz crystal microbalance (EQCM) studies have allowed for the direct determination of electrode mass, both during deposition and electrochemical performance evaluation, which has enabled analysis of electrode properties, including film growth (up to 26 $\mu g/cm^2$), density (~2 g/cm^3), and the charge storage during electrochemical cycling, including the rates of mass uptake/removal with charge. The characteristics of the composite electrodes were compared with PPy-only electrodes throughout.

1. Introduction

1.1. Energy storage in supercapacitor systems

Nowadays energy has emerged as a fundamental focus for major world economic powers and a great challenge for the scientific community [1]. Energy storage systems have in the past, and will continue to do so into the future, play a significant role in consumer electronics. They also have an emerging role in transportation, where the introduction of electric and hybrid electric vehicles is growing in popularity, and in grid energy storage, where they are an important complement to renewable energy production systems.

In this work our focus is on the use of supercapacitors for energy storage. The relative performance of supercapacitors compared to batteries and fuel cells can be summarized by a typical Ragone diagram [2]. Supercapacitors are typified by a high specific power output but a low specific energy density, which has unfortunately inhibited their widespread commercialization. Another distinct advantage that supercapacitors possess compared to other types of energy storage devices is their cyclability, which is typically of the order of >10^5 cycles, compared to ~10^3 for batteries. Considerable research in recent times has gone into improving the specific energy of supercapacitor electrode materials and devices, with the intent of also retaining their high specific power and excellent cyclability (e.g., [3–5]). Such developments will provide greater energy storage options for consumers.

1.2. Supercapacitor charge storage mechanisms and materials

Present day commercial supercapacitors typically employ a symmetrical geometry, in which both electrodes are based on high surface area carbons such as activated carbon, carbon fibres, aerogels, xerogels, fullerenes, and other various nanostructures [6,7]. The electrolyte in such systems is either a non-aqueous or aqueous electrolyte; e.g., 1 M tetraethylammonium tetrafluoroborate in acetonitrile or aqueous 1 M H_2SO_4, respectively. Energy storage in such devices occurs by charge separation at the solid–electrolyte interface within the porous electrode structure [8]. As a result of the use of a high surface area carbon materials, considerable charge can be stored; i.e., up to 300 F/g [8–10]. Furthermore, since no physical or chemical changes are occurring in the electrode with such a process, such systems exhibit excellent cyclability.

An alternative approach to charge storage in supercapacitor systems is to employ pseudo-capacitance, which is essentially the use of fast and reversible surface or near surface redox reactions [11]. Such an approach is a common strategy for improving specific capacitance due to the fact that more than just the surface of the material is being utilized for charge storage. Classes of materials that exhibit pseudo-capacitance include conductive polymers and metal oxides, with this latter class of materials crossing the boundary between battery and supercapacitor domains [12,13]. An

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http://dx.doi.org/10.1016/j.synthmet.2014.07.007
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excellent recent review of materials for supercapacitors by Naoi and Simon can be found in reference [13].

Conducting polymers that have been examined as supercapacitor electrode materials include polyaniline, polypyrrole and polythiophene, together with their many derivatives [14]. The specific capacitance of such materials has been reported to range up to ~300 F/g, with energy storage again occurring via charge separation at the conductive polymer–electrolyte interface [15]. One of the main drawbacks of these systems, however, is their poor mechanical stability after repeated cycling [16].

The prototypical metal oxide that has been examined as a supercapacitor electrode is hydrated amorphous ruthenium dioxide, which has been reported to have a specific capacitance of up to 1200 F/g [17,18]. While an excellent performing material, its high cost and toxicity has limited its widespread commercial uptake. As reported by Naoi and Simon, other metal oxides that have been examined include manganese, nickel, tin, and iron oxides [13]. Of these, it is apparent that manganese oxides have considerable potential as supercapacitor electrode materials, exhibiting good electrochemical performance (up to 800 F/g [13]), as well as being of low cost and toxicity. Recent reports from our own laboratory have shown that electrodeposited thin films of manganese dioxide exhibit excellent specific capacitances of over 2000 F/g in an aqueous 0.5 M Na_2SO_4 electrolyte [19]. This level of performance has been ascribed to the use of a high surface area active material exhibiting both pseudo-capacitance and charge separation at the solid–electrolyte interface.

1.3. This work

In the vast majority of work reported previously in the literature, the materials being examined have been prepared as free flowing powders, which were then cast into electrodes on a suitable conducting substrate. It is relatively rare that thin films of manganese dioxide, or any electro-active material for that matter, are deposited onto a substrate which was then used immediately as the supercapacitor electrode. This approach has considerable advantages, not only in terms of performance, but also in terms of ease of processing. A number of researchers have used electrodeposition to produce polypyrrole, manganese dioxide, and composites thereof (e.g., [20–25]); however, relatively thick deposits were studied in these reports which has ultimately influenced the performance results, making the electrodeposited films comparable in performance to powdered materials.

Conducting polymers such as polypyrrole can also be prepared via electrodeposition (e.g., [26]); however, similar to the electrodes prepared from powdered materials, their mechanical instability causes a breakdown in electrode performance [27]. In this work we will examine the electrochemical deposition of polypyrrole that has been modified by the presence of Mn^{2+}, with the intent of stabilizing the polypyrrole during cycling. Additionally, we will also demonstrate that enhanced electrode performance from these composites can be achieved through the use of thin film electrodeposition.

2. Experimental

2.1. Materials

The materials used in this study for the synthesis of the electrode composites were the pyrrole monomer (Py; Merck; 99%), $MnSO_4{\cdot}H_2O$ (Sigma–Aldrich; >99%) and H_2SO_4 (Sigma–Aldrich; 98%). Experiments to evaluate the electrochemical performance of our electrodes employed an aqueous solution of K_2SO_4 (Sigma–Aldrich; >99%). All aqueous solutions prepared in this study made use of Milli-Q ultra pure water (resistivity >18.2 MΩ.cm).

2.2. Electrochemical protocols

All electrochemical experiments were conducted using a Stanford Research Systems QCM200 as an electrochemical quartz crystal microbalance (EQCM). In this case the working electrode was a 1.325 cm^2 platinum disk sputter coated on a 5 MHz resonant frequency quartz crystal. Prior to use, this platinum electrode was cleaned by immersion in a 0.1 M H_2SO_4 + 5% H_2O_2 solution. This was used in conjunction with a saturated calomel reference electrode (SCE), against which all potentials were measured and reported, and a graphite rod counter electrode (6.3 cm^2). All electrochemical experiments were controlled using a Perkin Elmer VMP multi-channel potentiostat/galvanostat with ECLab software.

Electrodeposition experiments were carried out using aqueous solutions containing combinations of Py (0, 0.001, 0.01 or 0.1 M), $MnSO_4{\cdot}H_2O$ (0, 0.001, 0.01 or 0.1 M) and 0.1 M H_2SO_4. All electrodeposition experiments were carried out using chronoamperometry, although prior to this a linear sweep voltammetry experiment was conducted on each solution being studied so as to identify an appropriate step potential. Once this potential had been identified, and after the platinum substrate had been cleaned again in 0.1 M H_2SO_4 + 5% H_2O_2, each chronoamperometry experiment was carried out for 30 s.

After each chronoamperometric deposition, the coated quartz EQCM electrode was rinsed thoroughly with Milli-Q water to remove any associated plating electrolyte. Without being dried the electrode was then immersed into a 0.1 M K_2SO_4 solution, together with the same SCE reference and graphite counter electrodes as used previously. This electrode was then cycled for at least 50 cycles between 0.0 and 1.0 V vs SCE at a rate of 5 mV/s.

The Pt working electrode was used for electrochemical impedance spectroscopy work (EIS) work. After each electrodeposition, the Pt working electrode was rinsed H_2O and without being dried the electrode was then immersed into a 0.1 M K_2SO_4 solution, together with the same SCE reference and graphite counter electrodes in an EIS system by using the combination of a Solartron 1254 Frequency Response Analyzer and a Solartron 1287 Electrochemical Interface controlled by ZPlot software. From the open circuit voltage of the thin films electrode (0.300 V) the voltage was stepped in the anodic direction 25 mV, after which it was allowed to equilibrate for a period of 10 min. After this, an impedance spectrum on the thin films electrode was measured using the frequency range 20 kHz to 0.1 Hz and a 10 mV excitation signal. This sequence was repeated to the upper voltage limit (1.0 V vs SCE), down to the lower voltage limit (0.0 V vs SCE), and then once more back up to the upper voltage limit. The resultant impedance spectra were then interpreted using an appropriate equivalent circuit.

2.3. Morphological characterization

Owing to the nature of the very thin films of electrodeposited material, morphological characterization is quite challenging. Traditional methods of analysis such as X-ray diffraction and scanning electron microscopy (SEM) are not possible due to the limited amount of material present. Despite this, lengthening the deposition time to make a thicker deposit has shown that the material is still amorphous to X-ray diffraction [19]. There are however, concerns about this approach because of changes in the nature of the deposit using the chronoamperometric method. Nevertheless, for morphological characterization in this study the samples were examined by atomic force microscopy (AFM; Asylum Research Cypher Scanning Probe Microscope) in AC mode with a 2.44 Hz scan rate, transmission electron microscopy (TEM; JEOL JEM-1200EXII)