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Potentiostatically deposited polypyrrole/graphene decorated nano-manganese oxide ternary film for supercapacitors

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Abstract

A simple method based on potentiostatic polymerization was developed for the preparation of ternary manganese oxide-based nanocomposite films. The ternary nanocomposites, which were characterized using x-ray diffraction spectroscopy and x-ray photoelectron spectroscopy, showed that the manganese oxide within the film consisted of MnO_2 and Mn_2O_3. Electrochemical measurements showed that the ternary nanocomposite electrode exhibited high specific capacitance (up to 320.6 F/g), which was attributed to the morphology of a polypyrrole/graphene/manganese-oxide (PPy/GR/MnO_x) ternary nanocomposite. The experimental approach maximized the pseudocapacitive contribution from redox-active manganese oxide (MnO_x) and polypyrrole (PPy), as well as the electrochemical double layer capacitive (EDLC) characteristic from graphene (GR) sheets. Long cyclic measurements indicated that the specific capacitance of the ternary nanocomposite film could retain 93% of its initial value over 1000 charge/discharge cycles, in the potential range of −0.2 to 0.7 V versus silver/silver chloride electrode (Ag/AgCl).

Keywords: Supercapacitor; Manganese oxide; Graphene; Polypyrrole

1. Introduction

Supercapacitors have received considerable attention owing to their expanding array of applications, especially in providing power to hybrid vehicles and portable electronics. As energy storage devices, supercapacitors bridge the gap between a conventional capacitor and a battery [1], and have been studied extensively. In this context, relentless efforts have been underway, especially in searching for novel electrode materials. Generally, there are three categories of electrode materials, i.e. carbon materials, metal oxides/hydroxides and conducting polymers. Depending on the electrode materials used, two types of supercapacitors can be constructed; namely, electric double layer capacitors (EDLC) and pseudocapacitors. Energy storage in an EDLC results from the separation of electronic and ionic charges between the electrode and electrolyte interface, while a pseudocapacitor utilizes Faradaic reactions occurring within the active material of electrodes [2,3].

Carbon materials such as activated carbon and carbon nanotubes (CNT) have been investigated widely for EDLC, owing to their good conductivity and excellent chemical properties [4]. Recently, the focus has been diverted to graphene-based materials since they have shown immense theoretical and practical advantages, such as a large surface area, excellent conductivity and capacitance, as well as relatively low production costs [5–8]. On the other hand, polypyrrole (PPy), which is an ideal candidate for pseudocapacitor electrode, is receiving considerable attention as a result of its high electrical properties [9], ease of preparation,

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good environment stability [10] and large specific capacitance [11]. Redox metal oxides such as RuO_2 and MnO_2 are also promising materials for pseudo-capacitors. Hydrous RuO_2 has been studied extensively, and its capacitance value was as high as 720 F/g in acidic electrolyte, although the drawback of this material is its high production cost and toxic nature [12]. To circumvent these disadvantages, researchers have focused on other cost-effective and 'green' electrode materials. Correspondingly, the electrochemical behavior of MnO_2 is also a subject of intensive investigation, owing to its good electrochemical performance [13,14]. Moreover, MnO_2 has attracted considerable attention thanks to its abundance and relatively environmentally friendly nature.

Numerous material types have been identified as promising materials for supercapacitor electrodes. In essence, each class has its distinctive advantages and disadvantages, in terms of supercapacitor application. For example, the electrostatic charge storage mechanism of the EDLC electrode has very high stability during charge–discharge cycling. However, electrodes of this kind only store limited charges, leading to low specific capacitance [15]. While transition metal oxides and conducting polymers have relatively high capacitance, the challenges remain because the relatively low mechanical stability and cycle life inhibit their application for supercapacitors [16]. Hence, the real current challenge in the synthesis of binary or ternary composites of carbon materials, conducting polymers and metal oxides as materials for supercapacitors, is therefore to leverage their unique advantages while, at the same time, minimizing their disadvantages.

Recently, efforts have been made to integrate nano-scale manganese oxide onto graphene; however, the nanocomposite exhibits specific capacitances within the 100–200 F/g [13–18]. Based on the findings, it has shown some improvement in maximizing the utilization of manganese oxide, but substantial improvements still have to be made for its successful commercialization.

In this study, a simple, fast and one-step electrochemical polymerization of polypyrrole/graphene/manganese oxide ($PPy/GR/MnO_x$) ternary nanocomposite films was conducted, whereby they are deposited potentiostatically in the presence of sodium *p*-toluenesulfonate (NapTS) as a supporting electrolyte. In our previous study, graphene oxide (GO) was electrodeposited with a pyrrole monomer from an aqueous solution to form a polypyrrole/graphene (PPy/GR) nanocomposite film. It has been shown that GO was reduced to graphene (GR) during the deposition process [19]. For the present study, $PPy/GR/MnO_x$ ternary nanocomposites were synthesized potentiostatically, with the addition of $MnSO_4$ in the deposition solution. The manganese oxide (MnO_x) particles were grown directly along the PPy and conducting graphene, which acted as spacers to maintain the detachment of neighboring sheets. The graphene sheets, coated with MnO_x particles and PPy, overlapped with each other, forming a three-dimensional (3D) conducting network that improved the contact between the electrode material and the electrolyte (Fig. 1). To the best of the authors' knowledge, the deposition of 3D structured MnO_x directly onto graphene and PPy has not been previously reported. The obtained nanocomposite exhibited a high specific capacitance and an excellent long cycle life.

2. Experimental

2.1. Materials

Graphite powder was obtained from Ashbury Graphite Mills Inc., code no. 3061. Sulfuric acid (H_2SO_4, 95–98%), phosphoric acid (H_3PO_4, 85%), potassium permanganate ($KMnO_4$, 99.9%) and hydrogen peroxide (H_2O_2, 30%) were purchased from Systerm, Malaysia. Hydrogen chloride (HCl, 37%) and manganese sulfate ($MnSO_4$, 98–101%) were purchased from Sigma-Aldrich and Merck, respectively. Pyrrole (99%, Acros Organic) was stored in 0 °C and distilled prior to use.

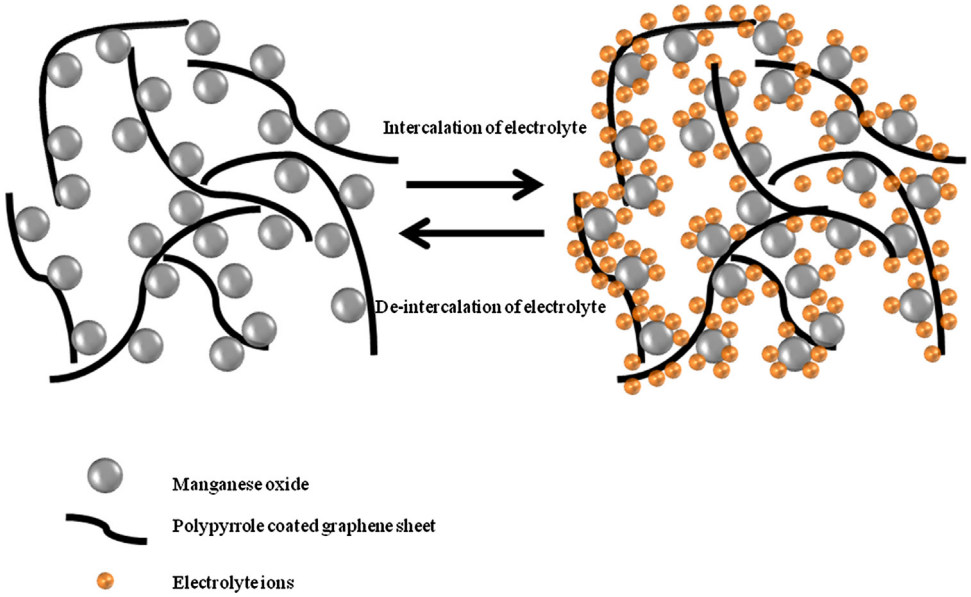

Fig. 1. 3D model of microstructure of ternary nanocomposite facilitating the diffusion of electrolyte ions.