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Manganese oxide/graphene oxide composites for high-energy aqueous asymmetric electrochemical capacitors

Charl J. Jafta[a,b,1], Funeka Nkosi[a,c], Lukas le Roux[a,2], Mkhulu K. Mathe[a,2], Mesfin Kebede[a], Katlego Makgopa[c], Yang Song[d], Dennis Tong[d], Munetaka Oyama[e,2], Ncholu Manyala[b], Shaowei Chen[d,**,2], Kenneth I. Ozoemena[a,c,*,2]

[a] Energy Materials, Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR), Pretoria 0001, South Africa
[b] Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials, University of Pretoria, Pretoria 0002, South Africa
[c] Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa
[d] Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA
[e] Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan

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ABSTRACT

A high-energy aqueous asymmetric electrochemical capacitor was developed using manganese dioxide (α-MnO_2)/graphene oxide (GO) nanocomposites. The nanostructured α-MnO_2 was prepared from micron-sized commercial electrolytic manganese dioxide (EMD) via a hydrothermal reaction in the presence and absence of sodium dodecylsulphate (SDS), α-$MnO_{2(SDS)}$ and α-MnO_2, respectively. Unlike the as-prepared α-MnO_2, the presence of SDS during the hydrothermal reaction conferred different morphologies on the intermediate precursors for the α-$MnO_{2(SDS)}$. Also, the XRD patterns showed that the α-$MnO_{2(SDS)}$ are more crystalline than the as-prepared α-MnO_2. The superior electrochemical performance of the α-$MnO_{2(SDS)}$/GO composite (280 $F g^{-1}$, 35 $Wh kg^{-1}$, and 7.5 $kW kg^{-1}$ at 0.5 $A g^{-1}$) coupled with excellent long cycle life clearly indicates that this electrode system has the potential of being developed as an efficient aqueous asymmetric electrochemical capacitor. The high performance of the α-$MnO_{2(SDS)}$/GO composite was interpreted in terms of the enhanced crystallinity of the α-$MnO_{2(SDS)}$. Interestingly, the electrochemical performance is comparable to or even better than those reported for the more conductive graphene/MnO_2 composites.

1. Introduction

Asymmetric electrochemical capacitors (ECs), also known as hybrid supercapacitors, are characterized by Faradaic reactions (pseudo-capacitance) and charge-storage (electrical double layer capacitance), and have begun to receive immense research interests because of their high energy density, large power density and long lifetime [1]. The use of aqueous electrolytes in asymmetric ECs is important due to several advantages of such systems [2], such as (i) simplicity of fabrication and packaging procedures that avoid rigorous environmental controls; (ii) a high degree of safety as compared to the use of organic-based ECs with respect to thermal stability and runaway; (iii) the use of low-toxicity and low-cost electrolytes; and (iv) specific energy that meets or exceeds those of non-aqueous EDLCs.

Toward this end, manganese dioxide (MnO_2) has been regarded as a promising active component for EC electrodes [3]. Electrolytic manganese oxide (EMD), on the other hand, does not show good capacitance. EMD is characterized by small surface areas and composed of a mixture of several crystallographic phases (α, β, γ, δ and λ). Of these, α-MnO_2 gives the best electrochemical capacitance [4]. South Africa has the largest manganese deposit in the world, and remains the major global supplier of EMD. One of the means of expanding the value chain of its manganese resource would be to find ways of exploiting EMD for energy storage systems. Therefore, there is a need to develop effective protocol whereby commercial EMD may be exploited to generate α-MnO_2 for electrochemical capacitor applications.

In addition, whereas activated carbons have been used extensively in the preparation of electrochemical capacitor electrodes [5–7], graphene and graphene oxide (GO) nanosheets are

* Corresponding author at: Energy Materials, Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR), Pretoria 0001, South Africa. Tel.: +27 128413664; fax: +27 128412135.
** Corresponding author. Tel.: +1 831 459 5841; fax: +1 831 459 2935.
E-mail addresses: shaowei@ucsc.edu (S. Chen), kozoemena@csir.co.za (K.I. Ozoemena).
[1] ISE student member.
[2] ISE member.

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beginning to be taunted as potential replacement due to their much enhanced energy densities. Theoretically, GO is not suitable for supercapacitor applications [8], but Xu et al. [9] recently showed that GO can exhibit higher capacitance than graphene due to the extra pseudo-capacitance effect of the attached oxygen-containing functional groups on its basal planes. Thus, in light of its higher capacitance, lower cost and shorter processing time than graphene, GO may become a better choice than graphene in electrochemical capacitor applications.

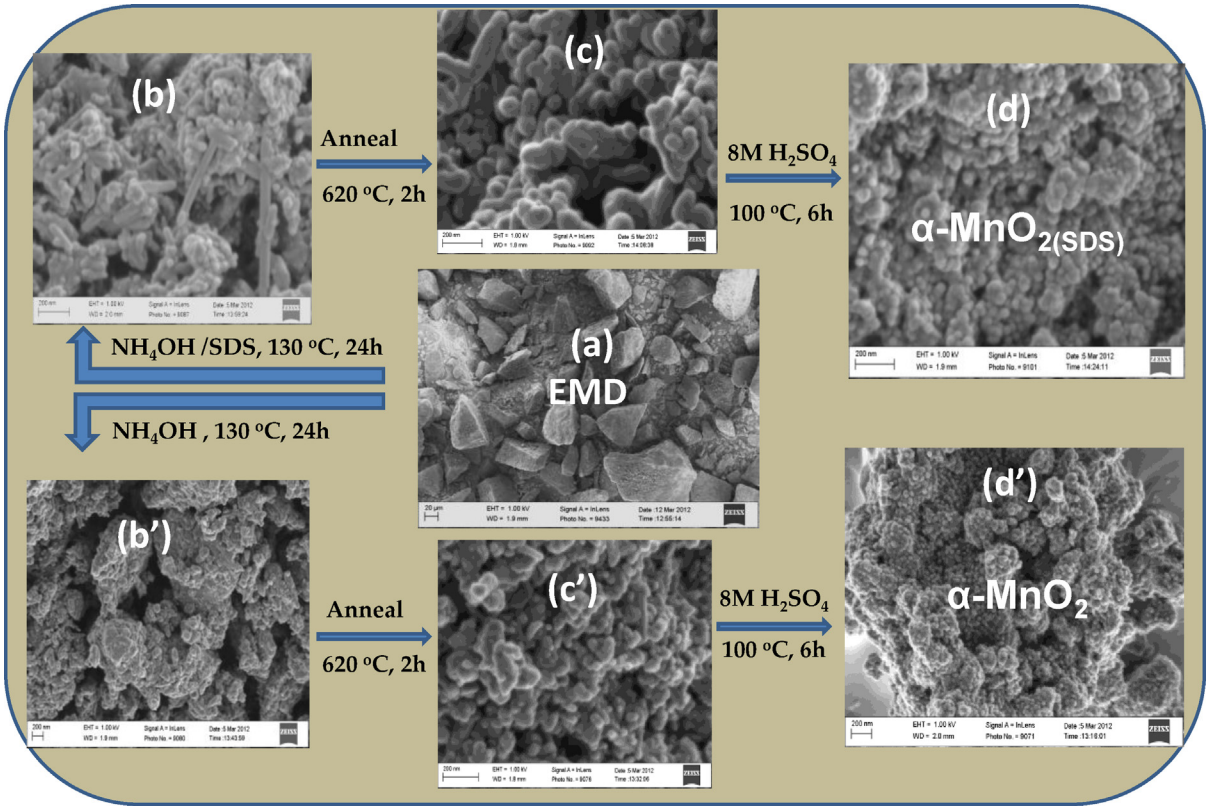
It is within such context that this study was carried out. In this communication we describe the properties of α-MnO_2/GO composite as a high-energy, high-power asymmetric electrochemical capacitor in neutral aqueous solutions. To our knowledge, this is the first study on the use of EMD-generated α-MnO_2/GO hybrids for asymmetric electrochemical capacitors in neutral aqueous electrolytes. We show that in aqueous electrolytes α-MnO_2/GO exhibits a high specific energy of 23–35 Wh kg^{-1} and high power density of 4.5–7.2 kW kg^{-1}, which are comparable to or even better than those reported for MnO_2/graphene asymmetric ECs reported in the literature [10–12]. In addition, the electrode shows excellent stability of over 1000 charge–discharge continuous cycles.

2. Experimental

2.1. Materials and procedure

Commercial electrolytic manganese dioxide (EMD) was obtained from a South African supplier, while sodium dodecylsulphate (SDS, 99%) was purchased from Sigma–Aldrich. The nanostructured α-MnO_2 was obtained from EMD via a hydrothermal reaction in the presence of SDS by slight modification of the literature method [13]. As summarized in Scheme 1, a mixture of 1 g of EMD, 1 g of SDS and 50 mL of 5% NH_4OH was stirred overnight and ultrasonicated for 30 min, transferred to a teflon-lined stainless steel beaker in an autoclave and heated at 130 °C for 24 h, then cooled to room temperature and washed several times with a copious amount of distilled water via centrifugation. The final product was dried overnight at 50 °C in a vacuum oven. These dried powders were then annealed at 620 °C for 2 h and subsequently subjected to an acid treatment to obtain the nanostructured α-$MnO_{2(SDS)}$. The acid treatment was carried out by reacting 10 mL of 8 M H_2SO_4 with 30 mg of the nanostructured Mn_2O_3 sample at ~100 °C for 6 h under continuous stirring, and then at room temperature for 16 h [13]. These samples were washed to a neutral pH with de-ionized water and then dehydrated at 300 °C to obtain the desired product. For comparison with the α-$MnO_{2(SDS)}$, another product (abbreviated herein as α-MnO_2) was obtained using the above method but without SDS.

GO was prepared using the modified Hummer's from graphite powders [14]. In brief, 0.5 g of graphite powders and 0.5 g of $NaNO_3$ were mixed with 23 mL of concentrated H_2SO_4 under magnetic stirring for 10 min in a clean flask at 0 °C. 3 g of $KMnO_4$ was then added slowly to the above solution over a 3 min period to prevent a sudden temperature increase. Then the dark greenish solution was transferred to a 35 ± 5 °C water bath and stirred for about 1 h. Next, 50 mL of water was added slowly, and the solution was stirred for another 30 min while the temperature was raised to 90 ± 5 °C. After adding 150 mL of water, 3 mL of H_2O_2 (30%) was added drop-wise, resulting in the formation of a brownish solution. Finally, the warm solution was filtered and washed with 50 mL of 0.1 M hydrochloric acid solution and 500 mL of water, respectively. The filter cake was then dispersed in water by sonication using a table-top ultrasonic cleaner (VWR B1500-A MTH, 50 W). The products were then separated via centrifugation for 5 min to remove all visible particles. The last sediment was re-dispersed in water under mild sonication, which resulted in a homogeneous brown solution of exfoliated



Scheme 1. The SDS-based and SDS-free routes for the preparation of α-$MnO_{2(SDS)}$ (d) and α-MnO_2 (d′) from EMD precursor (a) via intermediate nanostructures (b/b′) and (c/c′). Scale bars are 20 μm for (a), and 200 nm for structures (b/b′) to (d/d′).