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Simonkolleite-graphene foam composites and their superior electrochemical performance

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ABSTRACT

Simonkolleite-graphene foam (SimonK/GF) composite has been synthesized by a facile solvothermal and environmentally friendly technique with excellent electrochemical properties. The obtained product was initially analyzed by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), Fourier transform infrared resonance (FTIR) spectroscopy and cyclic voltammetry (CV) techniques. The microscopy results reveal hexagonal sheets interlaced with each other and adjacent graphene sheets. The existence of graphene foam in the simonK/GF composite is further confirmed from the structural and the optical characteristics obtained from XRD and FTIR respectively. The BET results obtained indicate an improvement in the surface area due to the addition of graphene foam to a value of 39.58 $m^2 g^{-1}$. The N_2 adsorption/desorption also shows the presence of active mesopores required for charge transport. As a promising electrode material for supercapacitors, the composite shows a high specific capacitance value of 1094 F/g at 1 A/g with a coulombic efficiency of 100% after 1000 cycles. These results show a potential for adoption of this composite in energy storage applications.

1. Introduction

In the developing field of energy storage technology, the design and fabrication of efficient energy storage devices with high energy and power densities are of growing concern today. Numerous scientists have engaged in active research to develop robust and reliable energy storage systems which will match the increasing demand for energy in a variety of applications from energy storage systems in portable hand-held devices to back-up systems in hybrid electric motor vehicles.

Supercapacitors (SCs) with high power densities and long cycle life as compared to much common hybrid batteries in use today are promising candidates for such applications. However, they are also characterized with low energy densities in comparison to batteries which creates a drawback for their wide applications [1]. The nature of the electrode material which makes up the SC is one of the most important factors that determine its performance.

Based on the device operation mechanism, SCs can be broadly divided into two classes; the electric double layer capacitors (EDLCs) and the pseudocapacitors [2]. In order to deal with the problem of low energy density, most recent studies include combining materials with pseudocapacitive and electric double layer capacitive (EDLC) properties [2–8]. This is achieved by combining high specific surface area carbonaceous materials (e.g. graphene [3,4], carbon nanotubes [5–7], activated carbon [8,9]) with transition metal oxides and hydroxides with good redox properties.

For example, Gao's research group illustrated the production of graphene nanosheet-layered double hydroxide (GNS/LDH) by a simple hydrothermal technique [3]. In the study, glucose was used as a reducing agent in place of toxic hydrazine to exfoliate graphene oxide (GO) and obtain an even dispersion of GNS in water. The observed remarkable specific capacitance was attributed to be due to the combination of electric double layer capacitance (EDLC) and Faradaic pseudocapacitance from the open structure system with improved contact between the electrode/electrolyte interface [3]. The conductive network of graphene sheets overlapping each other was reported to facilitate fast electron transfer between the active composite material and the charge collector. Another study by Fao et al., [8] reports a graphene/MnO_2 composite as positive electrode synthesized by microwave irradiation with activated carbon nanofibres (ACN) as negative electrode in an asymmetrical cell with Na_2SO_4 aqueous electrolyte. A maximum energy density of 51.1 Wh Kg^{-1} at a corresponding

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power density of 102.2 W kg^{-1} was obtained with excellent cycling stability retention of 97% after 1000 cycles. The observed device performance was attributed to the synergistic properties of both electrodes which provided an extended voltage window necessary for an improved energy density.

Recently, simonkolleites (SimonK, also known as zinc chloride hydroxide monohydrate, $Zn_5(OH)_8Cl_2 \cdot H_2O$) have received enormous attention due to their morphological properties composed of slabs and platelets suitable for numerous applications ranging from gas sensing [10] to materials for supercapacitor applications [11]. They also crystallize hexagonally with a perfect cleavage parallel to the (001) direction [12]. Similar to metal oxides, simonkolleites contain electrochemically active sites necessary for efficient charge storage. SimonK is electrically and chemically active due to the oxygen vacancies available on its surface, as in the case of ZnO. These vacancies may then act as n-type donors and subsequently improve the material's conductivity [10]. For supercapacitor applications, the abundance of a hexagonal microplatelet interactive network will likely provide the surface required for ionic surface interactions during operation. However, the pseudocapacitance of pristine simonK for energy storage is still low when compared with other metal oxides and hydroxides due to their lower electrical conductivity, lower surface area and tendency of the sheets to stack together. To overcome such limitations, efforts have been made by previous researchers to use carbon materials, such as graphene [3,11] or surfactants [13], to reduce the restacking and also improve the sheet thickness which would consequently improve the surface area and active porous sites for charge transport and storage.

The obtained hybrid system composed of simonkolleite-graphene will most likely have an improved electron transport rate, high electrolyte contact area for ion accessibility by creating more pores within the composite material. The combination of the graphene foam with simonkolleite microplatelets integrates the positive properties of electric double layer capacitance and pseudocapacitance. In addition, an in situ solvothermal synthesis approach of the simonK in the presence of evenly dispersed graphene foam leads to the synthesis of a simonkolleite-graphene foam composite (SimonK/GF) electrode with successful delamination/spacing of the simonkolleite sheets and will subsequently produce thinner sheets with improved surface properties and specific capacitance [4,14]. The in situ growth approach on a conductive substrate such as nickel-foam graphene ensures the simplification of the entire fabrication process and the direct acquisition of the composite electrode for device application. Although these are the desired properties for energy storage nanomaterials suitable for supercapacitors applications, limited studies have been done in this regards in relation to simonkolleite microplatelets.

In this present study, based on the considerations mentioned above, the synthesis of simonkolleite-graphene foam composite (SimonK/GF) is carried out with a subsequent study on the morphological, structural and electrochemical properties of the synthesized product. Analysis of the scanning microscopy images reveal relatively thin hexagonal sheets of simonkolleite interlaced with graphene sheets. Notably, the SimonK/GF composite showed an improved surface area with a superior electrochemical performance from cyclic voltammetry (CV) compared with SimonK alone. These results is a considerable improvement over earlier studies on simonkolleite structures for supercapacitor applications [11], wherein a similar in situ approach was adopted to grow simonkolleite on nickel foam-graphene template as electrode material for electrochemical applications. These results show the potential application of SimonK/GF composites as suitable electrodes for pseudocapacitors.

2. Experimental

2.1. Synthesis of nickel foam-graphene template and graphene foam

The nickel foam-graphene (NF-G) current collector was prepared by an atmospheric pressure chemical vapor deposition (AP-CVD) technique. Briefly, a known mass of compressed nickel foam template (Alantum, Munich, Germany), with an areal density of 420 g m^{-2} was placed in a quartz tube for the CVD growth of graphene. The nickel foam was first annealed at 1000 °C in the presence of Ar and H_2 gas for 60 minutes, prior to the introduction of the carbon source (CH_4 gas) at 968 °C. The flow rates of the gases Ar:H_2:CH_4 were 300:200:10 SCCM respectively. After 60 minutes of deposition, the samples were rapidly cooled by manually pushing the quartz tube to a lower temperature region to obtain the nickel foam-graphene.

In order to obtain the graphene foam, the samples were further immersed in 3.0 M HCl and placed on a hot plate at 60 °C to ensure complete etching of the nickel supporting structure. After complete etching of the nickel, the remaining graphene foam was washed several times in deionized water and dried in the oven to obtain the final graphene foam product.

2.2. In situ synthesis of simonkolleite-graphene foam composite

Simonkolleite-graphene foam composite was deposited directly on the NF-G template using an aqueous chemical growth technique whereby a solution containing equimolar portions of 2.974 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 0.588 g of sodium chloride (NaCl) and 4.102 g of hexamethylenetetramine ($C_6H_{12}N_4$, HMT) were first dissolved in deionized water. The next step involved adding 25 mg of graphene foam sonicated for 12 hours in water to the mixture prepared earlier and stirring the combined mixture with graphene foam for 15 minutes. Subsequently, the final mixture was transferred into a 150 ml Teflon-lined autoclave vessel and nickel foam-graphene substrate were immersed vertically into the reaction vessel kept at 110 °C for 19 hours. Thereafter, the autoclave was allowed to gradually cool down to ambient temperature. The final simonK/GF composite electrode was obtained after washing and drying at 60 °C.

The formation of simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) proceeds competitively in the solution following a set of successive chemical reactions as reported in our earlier publication [11]:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH^{4+} + OH^- \quad (2)$$

$$NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O \quad (3)$$

$$Zn\ (NO_3)_2{\cdot}6H_2O + H_2O \rightarrow Zn^{2+} + 2NO_3{}^- + 7H_2O \quad (4)$$

$$Zn^{2+} + 8OH^- + 2Cl^- + H_2O \rightarrow Zn_5(OH)_8Cl_2{\cdot}H_2O \quad (5)$$

Initially, HMT ($C_6H_{12}N_4$) disintegrates into formaldehyde (HCHO) and ammonia (NH_3). Ammonia tends to disintegrate deionized water to produce OH^- anions. Furthermore, NaCl disintegrates in water to form sodium cations (Na^+) and (Cl^-) chloride anions while Zn $(NO_3)_2 \cdot 6H_2O$ simultaneously disintegrates into zincate (Zn^{2+}) and nitrate ($NO_3{}^-$) ions. Lastly, OH^- and Cl^- anions react with Zn^{2+} cations to synthesize simonkolleite nanoplatelets ($Zn_5(OH)_8Cl_2 \cdot H_2O$).