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Study of mixed ternary transition metal ferrites as potential electrodes for supercapacitor applications

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ABSTRACT

Nanocrystallites of three mixed ternary transition metal ferrite (MTTMF) were prepared by a facile sol–gel method and adopted as electrode material for supercapacitors. The phase development of the samples was determined using Fourier transform infrared (FT-IR) and thermal gravimetric analysis (TG). X-ray diffraction (XRD) analysis revealed the formation of a single-phase spinel ferrite in $CuCoFe_2O_4$ (CuCoF), $NiCoFe_2O_4$ (NiCoF) and $NiCuFe_2O_4$ (NiCuF). The surface characteristics and elemental composition of the nanocomposites have been studied by means of field emission scanning electron microscopy (FESEM), as well as energy dispersive spectroscopy (EDS). The electrochemical performance of the nanomaterials was evaluated using a two-electrode configuration by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic technique in 1 M KOH electrolyte and was found to be in the order of: CuCoF > NiCoF > NiCuF. A maximum specific capacitance of 221 Fg^{-1} was obtained with CuCoF at a scan rate of 5 mV s^{-1}. In addition to an excellent cycling stability, an energy density of 7.9 kW kg^{-1} was obtained at a current density of 1 Ag^{-1}. The high electrochemical performance of the MTTMF nanocomposites obtained indicates that these materials are promising electrodes for supercapacitors.

Introduction

Electrochemical supercapacitors demonstrate promising potential in the field of energy storage due to their immense power density, excellent reversibility and high cycling stability [1,2]. Supercapacitors are able to provide high power and long cycle life in hybrid electric vehicles and uninterrupted power supplies [3]. Therefore, exploring new materials as potential supercapacitor electrodes is crucial in order to meet the requirements of high power density and long durability in the field of energy storage. Depending on the type of energy storage mechanism, supercapacitors can be classified into electrochemical capacitors (whereby the energy storage mechanism is based on electrochemical double layer consisting of carbon electrodes) and pseudocapacitors (which employ transition metal oxides or conducting polymers as electrode materials) [4–6].

Transition metal oxides are promising electrode materials for electrochemical supercapacitors. In general, transition metal oxides make use of fast and reversible faradaic redox reactions (pseudocapacitance) that involve ions and electrons in their charge storage mechanism. Various transition metal oxides such as ZnO, NiO, Co_3O_4, Fe_2O_3, RuO_2, MnO_2 and V_2O_5 have been investigated as active electrode materials for energy storage [7–14]. The expensiveness and high toxicity of RuO_2-based supercapacitors hinder its commercial application, while the relatively low specific capacitance as well as low electrical conductivity of cheaper transition metal oxides necessitate improvements [15].

Over the past decade, mixed metal oxides such as Ni/Mn oxide, Mn/Fe oxide as well as Mn/Ni/Co oxide have demonstrated tremendous improvements in electrochemical performance [16–18]. Spinel ferrites, MFe_2O_4, (where M = Mn, Co or Ni) are fascinating due to their impressive magnetic, electrical and optical properties as well as their ability of exhibiting different redox states and electrochemical stability [19–21]. The ferrospinel of general formula M^{2+} $[Fe^{3+}]\cdot O_4^{2-}$ possessing ferric ion in square bracket occupies the octahedral position and the metal ion outside the bracket occupies the tetrahedral site. M^{2+} represents the divalent ion such as Mn^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, etc. The breakthrough has been achieved when it is discovered that ferrites exhibit high permeability and the ability to exhibit several redox states which make them suitable electrode materials for supercapacitors [22]. Subsequently, several studies have been performed on ferrite systems such as nickel ferrite, cobalt ferrite, manganese ferrite as well

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as copper ferrite [23–25]. $MnFe_2O_4$ and $NiFe_2O_4$ are known to demonstrate superior pseudocapacitance [26–28]. It is expected that ferrite oxides (MFe_2O_4) may offer richer redox reactions, including contributions from both M and Fe ions, than those of the monometallic oxide. A promising approach to enhance the performance is designing novel ferrite-based hybrids. Ferrite spinels may also consist of a mixture of two divalent metal ions, in which the ratio of these divalent ions may vary and are referred to as mixed ferrites. The cation distribution of mixed ferrite significantly affects the surface properties of ferrospinels making them catalytically active. Because of their small size and large number of cations, for co-ordination sites, nanocrystallites are capable of enhancing the rate of chemical reactions and are increasingly gaining popularity as reactive nanocrystallites.

The preparation and electrochemical properties of $CoFe_2O_4$ nanomaterials have been reported by Deng et al. [29]. However, it is noted that pure $CoFe_2O_4$ cannot be conductive to yield satisfactory performance. A promising approach to improve the performance is the design of novel $CoFe_2O_4$-based hybrids. Spinel–nickel composites are also considered as attractive candidate for supercapacitor applications due to high theoretical specific capacitance, well defined redox behaviour, low cost and environmental benignity. Nickel ferrite ($NiFe_2O_4$), for instance, is an inverse spinel whereby Ni^{2+} occupies the octahedral site and half of the Fe^{3+} ions occupy the tetrahedral sites and is employed as anode material in lithium-ion batteries due to excellent electrochemical properties [30–33]. However, not a lot of research has been carried out on $NiFe_2O_4$ as a pseudocapacitive candidate.

Mixed ternary transition metal ferrites, $ABFe_2O_4$, (where A and B consist of a combination of Cu, Co or Ni) have not been explored as a potential candidate for supercapacitors to the best of our knowledge. Therefore, it is worthwhile investigating the suitability of nanocomposites comprising of copper cobalt ferrite (CuCoF), nickel cobalt ferrite (NiCoF) and nickel copper ferrite (NiCuF) in the challenging field of supercapacitors as potential electrode materials of high capacitance value. Furthermore, CuCoF, NiCoF and NiCuF can be promising for supercapacitors since they are inexpensive and innocuous materials.

The useful electrical properties of spinel ferrites are usually governed by the preparation conditions, chemical composition, sintering temperature, sintering time as well as doping additives [34]. Solution methods, in particular the sol–gel method, are employed because of its good stoichiometric control and the production of ultrafine particles in a relatively short processing time at lower temperatures.

In this investigation, we report a facile sol–gel method for the synthesis of mixed ternary transition metal ferrites (MTTMF) notably; copper cobalt ferrite (CuCoF), nickel cobalt ferrite (NiCoF) and nickel copper ferrite (NiCuF) nanocomposites using citric acid as a chelating agent. The synthesised nanocomposites are characterised for structural and surface morphological properties. The supercapacitive behaviour has been studied in 1 M KOH using cyclic voltammetry, galvanostatic charge discharge and AC impedance techniques.

Experimental

Materials

The starting materials were nitrates of copper, cobalt, nickel and ferrite as well as citric acid, all of analytical grade from Merck. Activated carbon (∝CH-0020) was purchased from RHE resources, isopropyl alcohol was obtained from Merck and potassium hydroxide (KOH) was purchased from R&M Chemicals. All chemicals were used as received without further purification. Deionised (DI) water (>18.4 MΩ cm^{-1}) from the Millipore system was used throughout the experiment.

Synthesis of MTTMF nanomaterials

The MTTMF nanomaterials were synthesised via a facile sol–gel method as illustrated in Fig. 1.

Stoichiometric amounts of metal nitrates (Table 1) were separately dissolved in 80 ml of deionised water and 20 ml of isopropyl alcohol. Citric acid was then added to the prepared aqueous solution to chelate the cations in the solution [35]. During this procedure, the solution was continuously stirred using an ultrasonic sonicator (UP400S) at a frequency of 0.5 cycles and amplitude of 50% in order to ensure homogeneity in the solutions. The solution mixture was then slowly evaporated on a magnetic stirrer at a temperature of 125 °C and speed of 150 rpm until a viscous gel was formed.

The thick slurry obtained was poured into ceramic boats for annealing in a tubular furnace. The dwell time and temperature set points of the furnace were increased at a ramping rate of 20 °C/min till 600 °C in order to remove the water, nitrate and carbon contents in the nanocomposite [35].

Sample characterisation

The surface characteristics and elemental composition of the composites were analysed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (FEI Quanta-400 FESEM) respectively. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the precursor gel were carried out at a heating rate of 10 °C/min in static air. The X-ray diffraction (XRD) patterns of the samples were observed by an X-ray diffractometer (XRD) (Philip XRD) operated at 33 mA and 45 kV with Cu Kα radiation (λ = 1.54056 Å) in the range of 10°–70° with step size 0.03°. N_2 adsorption/desorption was determined by the Brunauer–Emmett–Teller (BET) measurements using an ASAP-2020 surface area analyser. Infrared spectra (IR) for the gel precursor and the as-burnt powder were recorded on a PE883 spectrophotometer from 400 to 4000 cm^{-1} by the KBr pellet method.

Fabrication of electrodes and electrochemical measurements

The working electrodes for the supercapacitor were prepared using the following procedure: 70 wt.% of the synthesised nanomaterial were mixed with 20 wt.% of carbon black and 10 wt.% of polyvinyldifluoride (PVDF) prior to being dispersed in *N*-methyl-2-pyrrolidinone (NMP) to form a thick paste. The paste was then coated onto a single side of nitric acid treated aluminium sheet and dried at 70 °C for 7 h in a vacuum oven. The total weight of the active material in the electrode is usually ∼5 mg. For the fabrication of the carbon electrode, activated carbon was mixed with carbon black and PVDF in a mass ratio of 70:20:10 and a few drops of NMP.

The asymmetrical supercapacitor cell was assembled in a two-electrode configuration for the galvanostatic charge/discharge analysis to an Arbin Instrument (BT-2000) using the MITS Pro 4.0512.12 software. Constant current densities ranging from 1 to 10 Ag^{-1} have been employed for charging/discharging the cell in the voltage range 0–1 V. The cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were also studied in a two-electrode configuration using a VersaSTAT 3 (VE-400) electrochemical working station driven by the V3 studio version 1.0286 software. Cyclic voltammograms (CV) were recorded between 0 and 1 V w.r.t. reference electrode at a different scan rate (5–