Title: Nanostructured $Cd_{0.5}Cu_{0.5}Cr_xFe_{2-x}O_4$ / rGo ferrites electrode with ultra-long lifetime for electrochemical capacitors.

Abstract

The concentration of CO_2 in the atmosphere has risen dramatically over the last half-century. Since consistent measurements began in the 1950s, the current CO_2 concentration is the highest ever recorded. Green plants capture CO_2 directly from the air and convert it to reduced carbon species via sunlight-driven photosynthesis processes in nature. However, nature's photosynthesis processes are typically slow, and they are insufficient to offset the extremely large amount of CO_2 emitted by human activities[1]. Biological, thermochemical, photochemical, and electrochemical methods are currently being investigated as alternative CO_2 utilization approaches. The CO_2 electroreduction reaction is an appealing approach to achieving global carbon neutrality.

Therefore, the development of novel energy systems based on renewable energy sources is a must. To meet the urgent energy demand of electric vehicles and widely used energy storage devices, developing new generations of batteries and supercapacitors are the subjects of too many materials science researches. The capacitance and charge storage of supercapacitors are mainly dependent on the used electrode materials. In modern technology, supercapacitors receive a special place because they bridge the gap between batteries and conventional capacitors by delivering the stored energy in a fast and efficient way [3]. In supercapacitors capacitors (or electrochemical capacitors), energy may not be delivered via redox reactions and, thus the use of the terms anode and cathode may not be appropriate. By the orientation of electrolyte ions at the electrolyte/electrolyte interface, the so-called electrical double layers (EDLs) are formed and released, which results in a parallel movement of electrons in the external wire, that is, in the energy-delivering process[4].

Ferrites are basically ferrimagnetic oxides possessing very high resistivity and high permeability. The saturation magnetization of ferrite is less than half of ferromagnetic alloys, nevertheless they possess advantages such as applicability at higher frequencies, lower price, greater heat resistance, and higher corrosion resistance. Commercial application of ferrites had boosted since 1950 in electronics, and microwave devices. Magnetic response is dependent on size strongly, thus synthesizing different size particles may serve to tailor materials for desired applications. Ferrites can be classified according to their crystalline structure to four crystal types: spinel, garnet, magnetoplumbite, and orthoferrites. The first two have a cubic structure; the magnetoplumbite has a hexagonal structure, while orthoferrites have pervoskite structure and sometimes they are classified as a distinct class of materials, that is, "perovskites". The ferric ions in ferrites are the most important ions in these ionic compounds, having the formula M $^{2+}$ Fe₂ $^{+3}$ O₄ $^{2-}$, where M is a divalent metal ion such as Mn²⁺,Ni²⁺,Zn²⁺,Cd²⁺,Mg²⁺,Fe²⁺, and so on. By mixing two or more kinds of M²⁺ ions, one can formulate mixed ferrites to modify its physical properties according to the required applications. classical applications of bulk ferrites in electronics and high frequency transformers, the more recent applications of nano ferrites and their composites are so diverse and they are spreading more and more. These applications include; magnetic transducers-magnetostrictive, switches, electrodes, sensors, ferrofluids, electromagnetic wave shielding. Moreover, they are used for microwave devices, memory core, power transformers in electronics, antennas, read/write heads for high-speed digital tapes.

It has been found that the pure $CuFe_2O_4$ electrodes, suffers from low intrinsic electronic conductivity and huge volume change during charge/discharge processes, and shows low specific capacity and poor cycling stability. One of the effective approaches to improve the electrochemical performance of ferrites as anode materials is incorporating those transition metal oxide nanoparticles with carbon based materials.

Therefore, the aim of the present work is to synthesize, characterize and investigate the properties of nano-particle ferrite /graphene composites which are expected to be good candidates for electronics industry and energy storage applications. As a rapidly rising star on the horizon of materials science, graphene has already revealed its use in many potential applications. Because of its large specific surface area, remarkable electrical conductivity, excellent absorptivity, ultrathin thickness, superior structural flexibility, and high chemical and thermal stability, graphene has been received recent attention as a support for catalysts and advanced anode material of LIBs [3]. Graphene can be considered for potential applications in both emerging and conventional fields like field-effect transistors, electrochemical devices, electromechanical resonators, polymer nanocomposites, batteries, ultracapacitors, biosensors and light-emitting devices. Graphene-based flexible conducting electrodes are important for flexible electronic devices. They have been applied for organic light-emitting diodes (OLED), capacitive sensors in touch-screen displays and for organic photovoltaic (OPV) devices. Graphene and graphene- based hybrids can be considered as potential candidates for replacing Si-based technologies due to their extraordinary properties. Graphene can be a revolutionary material for living beings as it is less toxic, which can be manipulated chemically and, more importantly, it is biodegradable [5].

Because of their high theoretical capacity, binary transition metal oxides (BTMOs) have the potential to be supercapacitor materials. Electrochemical analysis was used to evaluate the performance of the nano-engineered products as supercapacitor electrode materials. The electrochemical results from cyclic voltammetry and galvanostatic charge-discharge spectroscopy demonstrated the prepared electrodes' enormous potential for supercapacitor applications. Here we will propose to investigate the ferrites/ rGo supercapacitor cathodes, which is expected to be a promising long-term cycling and rate performances. In particular, we propose to focus on the CV test at a potentialrange of -0.9-0 V under different scanning rates. Ex-situ x-ray absorption measurements will be performed at the binary transition metal oxides (BTMOs) L-edge to address directly the charge compensation mechanism and the evolution of the strains induced by the different networks during the electrochemical test. A complete characterization of the hybrid samples will be performed via XMCD at three different energies at the L₃ edge and (X-ray absorption spectra) XAS. We will take the advantage to combine the complementary information obtainable from temperature dependent extended XAS low energy secondary electrons at the BTMOs L_{3,2} absorption edge. The proposed experiment requires an experimental station with a high photon flux and a tunable energy range to be able to investigate the binary BTMOs L-edge. With the wide available energy range and high photon flux BM08 - ID11L - HESEB beamline, results highly appropriate for such experiment.