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Electrosynthesis of polypyrrole-vanadium oxide composites on graphite electrode in acetonitrile in the presence of carboxymethyl cellulose for electrochemical supercapacitors

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ABSTRACT

One-step electrochemical synthesis of polypyrrole-vanadium oxide (PPy-VOx) composites was performed on the Vanadium-intercalated pencil graphite (PG) surface in an acetonitrile solution with the presence of carboxymethyl cellulose (CMC). Both intercalated surface and composite coating were characterized using SEM-EDX Spectroscopy and X-Ray Diffraction (XRD) techniques. The capacitive properties of the coating were elaborated in an H_2SO_4/water medium using galvanostatic charge–discharge, potential cycling, and electrochemical impedance spectroscopy methods in comparison with the coatings prepared without additives. While V-intercalation provides a significant increase in the specific capacitance, the carboxymethyl cellulose enhances the cyclic performance of the composite. The improvement at the capacitance of the composite may be due to the homogenous distribution as well as the synergetic effect between PPy and VO_x. The capacitive properties were studied in aqueous solutions of H_2SO_4 and Li_2SO_4, and in an acetonitrile solution of HBF_4/$TBABF_4$. The specific capacitance value of the composite coating on the V-intercalated pencil graphite was determined as 204 F g^{-1} in an acetonitrile solution of HBF_4/$TBABF_4$ for a mass loading of 10.0 mg cm^{-2} at 2.0 A g^{-1}, when the capacitance of bare graphite was subtracted. The two-electrode supercapacitors composed of both asymmetric and symmetric configurations were also prepared and examined in an acetonitrile/adiponitrile solution of HBF_4/$TBABF_4$. The charge–discharge results for asymmetric supercapacitor reveal that the PPy-VO_x-CMC composite coating (20 mg cm^{-2}) on V-intercalated graphite paper represents a high energy density of 18 Wh.kg^{-1} and a high power density of 0.43 kW kg^{-1} at 0.5 A g^{-1}, as well as a stable cycle life at the potential range of 1.2 V.

1. Introduction

Metal oxides, such as manganese oxide, vanadium oxide, and cobalt oxide, and conducting polymers such as polyaniline and polypyrrole (PPy), represent a recently arising topic in supercapacitor research [1]. PPy is a candidate material for supercapacitor electrodes with high electrical conductivity, reversible electrochemical redox property, high charge storage capacity and good environmental stability. The specific capacitance values of PPy coated electrodes have been observed at a range of 179 F g^{-1} to 506 F g^{-1} at 10.0 mV s^{-1} scan rate [2–6]. These values are much greater as compared to the activated carbon electrodes, which are widely available in commercial products. On the other hand, more expensive and rare metals, such as RuO_2 [7,8], Co_3O_4 [9–11], NiO [12,13], MnO_2 [14–19] show better specific capacitance values.

Transition metal oxides have been subject to detailed research as an electrode material for electrochemical capacitors. Vanadium based electrodes exhibit excellent specific capacitance as well as stable electrochemical reversibility, good conductivity, long cycle life and typical layered structure [1,20]. Owing to these characteristics, vanadium oxides are promising active materials for high power/energy density. VO_2 has poor electrical conductivity and structural stability; therefore, long-term cycling stability is limited. The typical layered structures and multiple stable oxidation states (IV–V) of vanadium oxides (VO_x) represent critical factors improving the charge storage capacity when compared to the most

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of the transition-metal oxides. Vanadium oxides are capable of storing charge in a broad range of potential windows. There are several methods successfully utilized to prepare vanadium based electrodes, including electrodeposition [21–23], sol-gel hydrothermal/solvothermal template [24], electrospinning [25], and atomic layer deposition [24].

Hybridizing the metal oxides with highly conductive materials, such as graphene, carbon nanotubes, or conductive polymers is an effective method to improve the electrical conductivity and mechanical properties of materials [23,26]. PPy-Vanadium oxide composites for lithium-ion batteries and supercapacitors have been subjected to several studies [9,23,27–30]. The energy densities of the batteries have been reported over a range of 95.2–297 mAh.g^{-1}. The active materials of these electrodes were prepared chemically and then were mixed with carbon black using binders. For electrochemical supercapacitors, the composite materials were usually synthesized chemically, and they have the energy density of 20.0–69.2 Wh kg^{-1} and the power density of 0.162–0.72 kW kg^{-1} [28,30–32]. Bai et al. studied the electrochemical synthesis of the V_2O_5–PPy composite film on carbon cloth in an aqueous solution. The composite film was deposited via potentiostatic method at 0.7 V vs SCE from a 100 mM phosphate buffer solution (pH 6.86) containing 100 mM $LiClO_4$, 100 mM vanadyl sulfate and 30 mM pyrrole. The specific capacitance, energy density and power density of three electrode system were found as 412 F g^{-1}, 82 Wh kg^{-1}, 0.8 kW kg^{-1} at a current density of 4.5 mA cm^{-2}, respectively. 80% of the specific capacitance was maintained after 5000 galvanostatic charge–discharge cycles.

This study, for the first time in the literature, presents electrochemical codeposition of PPy and VO_x as a composite on vanadium intercalated graphite substrate in one-step in the presence of carboxymethyl cellulose. Via this method, VOx can be homogeneously encapsulated in the conducting PPy coating without using a binder. The electrochemical synthesis of the coatings on an intercalated substrate is a new study for supercapacitor research. Moreover, the electropolymerization medium is a nonaqueous acetonitrile solution. According to the previous studies, the conductivity (and thus the specific capacitance) of PPy synthesized in nonaqueous solutions is higher than that of aqueous solutions [33,34]. Both intercalated surface and composite coating were characterized by X-Ray Diffraction (XRD), Raman, SEM-EDX Spectroscopy techniques. The characteristics of composite film were compared with PPy films prepared under the same conditions. The capacitive properties of the coatings were investigated in aqueous H_2SO_4 solution, utilizing potential cyclic, galvanostatic charge–discharge measurements and electrochemical impedance spectroscopy (EIS) studies. A detailed electrochemical study for two-electrode supercapacitor with both asymmetric and symmetric configurations was also carried out in a non-aqueous electrolyte.

2. Experimental

2.1. Chemicals

Vanadium pentoxide (V_2O_5, Sigma), tetrabutylammonium tetrafluoroborate ($TBABF_4$, Sigma), tetrabutylammonium perchlorate ($TBAClO_4$, Sigma), lithium sulfate (Li_2SO_4), Triton X100 (Sigma), acetonitrile (HPLC–grade, Sigma), adiponitrile (Merk), perchloric acid ($HClO_4$, Merck), sulfuric acid (H_2SO_4, Fluka), tetrafluoroboric acid diethyl ether complex ($HBF_4{\cdot}O(CH_2CH_3)_2$, Sigma), oxalic acid ($H_2C_2O_4$, Sigma) and N-methyl-2-pyrrolidone (Sigma) and Carbon black (Sigma) were analytical grades and used as received without further purification. Pyrrole (Py, Fluka) was distilled under the cover of high purity nitrogen (Linde) and then stored in a refrigerator before use. Vanadium pentoxide, oxalic acid (in aqueous solution) and $HBF_4{\cdot}O(CH_2CH_3)_2$ or $HClO_4$ were used to extract vanadyl tetrafluoroborate ($VO(BF_4)_2$) or vanadyl perchlorate ($VO(ClO_4)_2$).

2.2. Characterization

The microstructure and morphology were characterized by field emission scanning electron microscope (FESEM, NOVA NANOSEM 650/FEI, USA), and energy-dispersive X-ray analysis (EDX) and elemental mapping (AMETEK-EDAX, USA). The coatings were examined by grazing incidence X-ray diffraction (XRD) analysis (PANalytical/EMPYREAN, USA) with Cu K_α radiation operating at 45 kV and 40 mA. The Raman measurements were performed using a DeltaNu Examiner Raman microscope (DeltaNu Inc., Laramie, WY, USA) with a 785-nm laser source, a motorized microscope stage sample holder, and a charge-coupled device detector. During the measurements, a 20× objective was used, and the laser spot diameter was 3.0 μm. Samples were measured with the laser power of 140 mW for 10 s acquisition time.

2.3. Electrochemical deposition and tests

Electrochemical measurements were carried out under the nitrogen atmosphere in a three–electrode cell with separate compartments for reference and counter electrodes. Reference electrodes were Ag/AgCl in acetonitrile and saturated calomel reference electrode (SCE) in aqueous solutions, whereas counter electrode was Pt spiral. Pencil graphite electrode (0.0244 cm^2), graphite sheet (2.00 cm^2, Ringsdorff-Werke) and graphite paper (0.196 cm^2, SGL Carbon GDL 39 AA) were used as working electrodes. Before the use, working electrodes were rinsed with acetonitrile and dried at room temperature. PPy was synthesized using potentiodynamic and galvanostatic methods in an acetonitrile solution containing 25 mM Py, 25 mM $TBABF_4$ (or $TBAClO_4$), 100 mM H_2O and with and without 25 mM HBF_4, (or $HClO_4$). For comparison of potentiodynamic and galvanostatic methods, the composite materials were deposited in the above acetonitrile solution, additionally containing 10 mM $VO(BF_4)_2$. The effects of additives were investigated using the galvanostatic method in the same acetonitrile solution with and without 25 mM TX100 and 0.5 mg/mL CMC. After the optimum concentrations of the chemicals were obtained, in the following sections, composite materials were galvanostatically deposited on V-intercalated pencil graphite, graphite sheet or graphite paper electrodes in the acetonitrile solution containing 25 mM Py, 25 mM $TBABF_4$ and 25 mM HBF_4, 10 mM $VO(BF_4)_2$, 100 mM H_2O, 25 mM TX100 and 0.5 mg/mL CMC. Electrochemical intercalation of vanadium into PG was performed by scanning the potential between 0.0 and −2.0 V vs. Ag/AgCl with a scan rate of 100 mV s^{-1} prior to the electrodeposition of the composite film in the polymerization solution, containing 25 mM Py, 25 mM $TBABF_4$, 10 mM $VO(BF_4)_2$, 100 mM H_2O, 25 mM HBF_4, 25 mM TX100 and 0.5 mg/mL CMC. After the deposition processes, the coatings were cleaned with acetonitrile to remove unreacted monomer molecules and dried under nitrogen flow at 25^{O}C for approximately 5 min. The electrochemical performances of coated electrodes were characterized using potential cycling, galvanostatic charge–discharge and impedance spectroscopy tests (EIS) in various electrolytes. In addition to these, analytical measurements were conducted for symmetric and asymmetric supercapacitor configurations. The galvanostatic measurement of the cell was characterized at current densities varying from 1 to 20 mA cm^{-2}. The cyclic stability measurement was carried out for 5000 cycles. Electrochemical impedance spectroscopy was measured at a frequency range varying from 0.01 to 100 kHz at open circuit potential. ZSimpwin V3.50 software (Scribner