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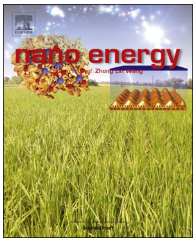

COMMUNICATION

Charge storage in KCu_7S_4 as redox active material for a flexible all-solid-state supercapacitor

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Abstract
Supercapacitors are promising devices for highly efficient energy storage and power management. A notable improvement in performance has been achieved through recent advances in understanding charge storage mechanism and the development of advanced nanostructured materials. Here, by combining experimental and theoretical investigations, we have unveiled the detailed charge storage mechanism of KCu_7S_4 wires based on a flexible all-solid-state supercapacitor. KCu_7S_4 with a unique double-tunnel structure and excellent conductivity exhibits outstanding properties as an electrode material in supercapacitors. Both electrochemical experiments and DFT calculations show that the stable energy storage process is mainly contributed by potassium ions' insertion/extraction, where potassium ions are proved to have been more active than lithium ions in the redox reactions on the KCu_7S_4 electrodes. The flexible supercapacitor based on the KCu_7S_4/Graphene paper is low-cost, easy to fabricate and environmentally friendly. The understanding for the charge storage presented in this work would guide the improvement on supercapacitor and exploration of new electrode materials.

Introduction

Recently, three-dimensional tunnel structure nanomaterials have attracted great interest in energy storage devices due to their attractive properties of high surface-to-volume ratio, high porosity and low coefficients of thermal expansion [1,2]. Especially for supercapacitors (SCs), tunnel

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structures with high surface areas and suitable mesopores can provide rich electroactive sites and short diffusion paths for charge carriers, which are required in the Faradaic redox reactions [3,4]. The electrode materials with larger tunnel structures, such as α-MnO_2 [5,6], Mn_3O_4 [5,7], and KCu_7S_4 [8], exhibit excellent electrochemical behavior during the charging/discharging process, which have been widely studied for SCs. Particularly, the novel KCu_7S_4 nanomaterial, one of the most promising electrode materials for supercapacitors, shows great pseudocapacitive behavior due to its double tunnel structure and good electronic conductivity [8,9]. Similar to α-MnO_2, the lattice structure of KCu_7S_4 is composed of Cu–S framework that contains pseudo-one-dimensional tunnels in which K ions reside [9,10]. These large tunnels not only increase effective space for insertion and extraction of ions, but also decrease ionic effective diffusion path [2]. Because of their great pseudocapacitive behavior, the tunnel structure nanomaterials have attracted more attention than other types of electrode materials [5,11]. However, most of investigations of these materials, including KCu_7S_4 [9,12], have mainly focused on the fabrication of hybrid structures of the electrodes and their electrochemical performance. A detailed charge storage mechanism of tunnel-structure materials is expected to be the scientific basis for further exploration of new pseudocapacitive materials or hybrid structures with excellent electrochemical behavior.

Although the KCu_7S_4 with a wire-like morphology shows great pseudocapacitive performance, the charge storage mechanisms in pseudo-capacitors involved redox reaction are still predictions proposed in our previous work [8,9]. Therefore, the details of charge storage mechanisms of the pseudo-capacitors involved redox reaction as well as insertion of cations on the surface of the KCu_7S_4 wires or into its interior tunnels need to be fully understood. Clarifying the transportation of K^+ and Li^+ in the KCu_7S_4 tunnels is significantly important for further improvements on such supercapacitor energy storage, and would also be instructive in exploring new electrode materials of SCs in the future.

Herein, we investigate the detailed mechanism of K^+, Li^+ and H^+ at atomic level by the first principles calculations based on density functional theory (DFT) [13,14] and the nudged elastic band method [15] is used to conduct the calculations of ions' diffusion in the KCu_7S_4 tunnels. The diffusion paths of Li^+ and K^+ are very close, both of which directly transfer along the tunnels and leave only one saddle point between the energy minimums with barriers of 0.3 eV and 0.73 eV respectively. However, the diffusion path of H^+ is much more complex due to its relatively stronger covalent bonds formed by binding sulfur ions, and a higher active energy of 1.5 eV is expected when the H-S bonds are broken. Moreover, in order to investigate the mechanism of functional ions between electrolytes and KCu_7S_4 electrodes, we have carried out theoretical analysis which combined DFT calculations and thermodynamic analysis. The potassium ions are much more active than lithium ions in the reaction of KCu_7S_4 tunnels, and a small amount of potassium ions will dominate the intercalation/deintercalation during the charging/discharging process. Meanwhile, we first find that the protons have very close activity with potassium ions, which is the reason of the higher current observed in the first few cycles, and the highest specific capacitance of 483 F g^{-1} achieved in the H_3PO_4 electrolyte. However the protons cannot be easily deintercalated from the KCu_7S_4 tunnels because the protons are bound to sulfur ions with covalent bonds, and leaving relative higher diffusion barrier. Therefore, the peak current will greatly decrease with the increase in cycles. Furthermore, we have fabricated a flexible all-solid-state SC device based on the KCu_7S_4/Graphene paper for the first time, and the device exhibits excellent electrochemical performance and good stability, revealing its enormous potential in energy storage.

Experimental section

Preparation of graphene paper

Graphene (Nanjing Corfu Nanotechnology Co. Ltd.) was used here as purchased. Firstly, graphene powder was dispersed in deionized water with 0.2 mg mL^{-1} for about 2 h by an ultrasonic instrument. The fabrication of graphene paper started with vacuum filtration of the prepared graphene dispersion by using the filter paper. Then, the graphene was uniformly dispersed on the filter paper. After drying it in oven at 60 °C for about 10 min, the graphene sheet was pressed at 5 MPa with laminator, which ensured strong adhesion between graphene and the paper and kept the surface of the graphene paper flat. In addition, the mass and resistance of the graphene paper were measured for many times until the graphene paper with required mass and resistance (about 3 mg cm^{-2} and 0.18 Ω cm^{-2}).

Fabrication of the KCu_7S_4/Graphene paper SCs

The KCu_7S_4 wires were synthesized by the hydrothermal method, which was reported previously [8]. The prepared KCu_7S_4 wires were first coated on the surface of the graphene paper electrodes. Then the KCu_7S_4/GP SCs were assembled by two pieces of identical KCu_7S_4/Graphene paper electrodes (work area: 2 cm × 4 cm) with a separator (Whatman 8 μm filter paper) sandwiched between. LiCl-PVA, KCl-PVA and H_3PO_4-PVA gel were used as electrolytes respectively. The LiCl-PVA, KCl-PVA and H_3PO_4-PVA electrolytes were prepared by mixing 12 g $LiCl \cdot 2H_2O$, 6 g KCl and 6 g H_3PO_4 respectively with 6 g PVA powder and 60 ml deionized water, and then heated to 85 °C until the solution became clear, and then the solution was kept under this condition for several hours and then cooled down.

Characterization and the electrochemical measurement

The morphology, chemical composition, and the structure of the products were observed under field-emission scanning electron microscopy (Nova 400 Nano SEM). Raman spectrometer investigations were performed by using Witec Confocal Raman microscopy (Lab RAM HR Evolution). The CV and GCD measurements were conducted with an electrochemical workstation (CHI 660D). An X-ray photoelectron spectrometer (XPS) analysis was performed on an ESCA Lab MKII using Mg Ka as the exciting source. *I-V* curve was measured