Potassium-doped copper oxide nanoparticles synthesized by a solvothermal method as an anode material for high-performance lithium ion secondary battery

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ABSTRACT

A simple and efficient approach was developed to synthesize CuO nanoparticles with improved electrochemical performance. Potassium (K^+)-doped CuO nanoparticles were synthesized by a simple and cost-effective solvothermal method followed by annealing at 500 °C for 5 h under air atmosphere. For comparison, an undoped CuO sample was also synthesized under the same conditions. X-ray diffraction analysis demonstrates that the K^+ ion doping caused no change in the phase structure, and highly crystalline $K_xCu_{1-x}O_{1-\delta}$ ($x = 0.10$) powder without any impurity was obtained. As an anode material for a lithium ion battery, the K^+-doped CuO nanoparticle electrode exhibited better capacity retention with a reversible capacity of over 354.6 mA h g^{-1} for up to 30 cycles at 0.1 C, as well as a high charge capacity of 162.3 mA h g^{-1} at a high current rate of 3.2 C, in comparison to an undoped CuO electrode (275.9 mA h g^{-1} at 0.1 C and 68.9 mA h g^{-1} at 3.2 C). The high rate capability and better cycleability of the doped electrode can be attributed to the influence of the K^+ ion nanostructure on the increased electronic conductivity, diffusion efficiency, and kinetic properties of CuO during the lithiation and delithiation process.

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Introduction

Copper oxide (CuO) is a well-known p-type semiconductor material with a low band gap of 1.2 eV. CuO has been employed for gas sensors, solar energy conversion, photocatalysis, optical switching, heterogeneous catalysis, and lithium-ion batteries (LIBs) [1–4]. CuO is noteworthy as a possible anode material for LIBs applications due to its low-cost, ease of synthesis, high theoretical capacity (670 mA h g^{-1}), and high safety. The storage of Li in CuO can be expressed as: $CuO + 2 Li^+ + 2 e^- \leftrightarrow Cu + Li_2O$, and the obtained theoretical capacity is 2 times larger than that of commercial graphite anode material. Unfortunately, its noticeable disadvantages, including low conductivity and large volume changes during the cycling process, make it difficult to meet the demands of high rate capability and a long-term life cycle [5,6]. In these respects, attention has been drawn to studying nanostructured electrodes in order to improve the electrochemical performance and structural stability. Nanostructured CuO not-only enables easy diffusion of Li$^+$ ions, but the strain associated with Li$^+$ ion uptake could also be

well accommodated, contributing to better electrochemical cycling performances. As a result, great efforts have been made to prepare various types of CuO nanostructures, which include nanoparticles [7], nanowires [8], nanorods (1D) [9], nanosheets (2D) [10], and 3D hollow nanostructures [11] with an aim to achieve optimized electrochemical performance of CuO. In addition, some other techniques have also been reported to improve the CuO anode performance. For example, by combining the metal oxides with graphene nanosheets, the nanocomposites exhibit both high capacity and capacity retention as anode materials in LIBs [3,12,13]. However, carbon containing hybrids generally exhibit relatively low specific capacity compared to pure metal oxides owing to the presence of carbon, as well as a low theoretical capacity. Therefore, to maintain high reversible capacity combined with high coulombic efficiency, achieving long cycling stability and good rate capability of the CuO electrode material still remains a challenging issue. Hence, it is fundamentally important to develop a new strategy that can accommodate CuO nanostructures with sufficient space to sustain the volume change from Li$^+$ ion uptake and release, which may provide useful hints for many types of oxide nanostructures to find applications in high-performance LIBs.

In the present work, a unique strategy to improve the electrochemical performance of CuO nanostructure by novel potassium ion (K^+) doping is reported. The optimized K^+-doped CuO

nanostructure ($K_xCu_{1-x}O_{1-\delta}$, $x = 0.10$) was synthesized using a cost-effective precursor and low-temperature solvothermal method in polyol medium. The polyol process has many advantages since it allows for nanoscale synthesis at lower synthesis temperatures and short-term heat treatment. The K^+ ion doping significantly improves the electrical conductivity, decreases the charge transfer resistance, and provides a large surface-to-volume ratio, which offers better electrochemical performances of the doped sample.

Experimental

Preparation of K^+-doped CuO and undoped CuO

In a typical synthesis, copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$, 99%, Junsei Chemical Co. Ltd., Japan], potassium nitrate (KNO_3, 99.999%, Sigma-Aldrich, USA) and diethylene glycol [$C_4H_{10}O_3$, 99%, Dae-Jung Chemicals, South Korea] were used without further purification. The detailed synthesis process can be found in our previous papers [14,15]. Briefly, the calculated amount of $Cu(NO_3)_2 \cdot 3H_2O$ was initially dissolved in 30 ml of diethylene glycol. Then, a calculated and optimized amount of KNO_3 (10 wt%) was slowly added to the obtained solution under continuous stirring, and after 5 h, a clear homogenous suspension was obtained. The reaction mixture was then transferred into a Teflon-lined bomb with a capacity of 40 mL and kept for solvothermal treatment in a drying oven pre-heated at 235 °C for 16 h. After natural cooling to room temperature, the product was ultrasonicated, washed with acetone several times to remove residual organic constituents before filtering, and finally dried under vacuum at 120 °C for 12 h. The obtained sample was thoroughly ground using an agate mortar and annealed at 500 °C for 5 h in air to increase the crystallinity of the sample. The undoped CuO sample was synthesized and annealed under the same conditions without the addition of KNO_3 for comparison. The final annealed samples were used to investigate the electrochemical performance.

Structure and morphology characterizations

The structure and morphology of the annealed undoped CuO and K^+-doped CuO samples were analyzed by X-ray diffraction (XRD, Shimadzu X-ray diffractometer with Cu-$K\alpha$ radiation, $\lambda = 1.5406$ Å), field-emission scanning electron microscopy (FE-SEM, S-4700 Hitachi), and field-emission transmission electron microscopy (FE-TEM, Philips Tecnai F20 at 200 kV in KBSI). For FE-TEM characterization, the samples were first dipped in ethanol and dispersed by ultrasonic vibration before coating onto copper grids. The EDX mapping was done on a Hitachi S-4700 FE-SEM equipped with an energy-dispersive X-ray analyzer (EMAX Energy EX-200, Horiba). In order to establish the valence states of K and Cu, the annealed sample of K^+-doped CuO was examined by X-ray photoelectron spectroscopy (XPS) using a Thermo VG Scientific instrument, Multilab 2000. XPS measurements were carried out using a dual anode X-ray source Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). The spectrometer was calibrated with respect to the C-1s peak (binding energy 285 eV).

Electrochemical measurements

The working electrodes were prepared by mixing the active material, super-P, and polyvinylidene fluoride binder with a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone solvent to form a slurry. The resulting slurry was coated onto a copper foil current collector and dried under vacuum at 80 °C overnight. The slurry was punched into circular electrodes after pressing between stainless steel twin
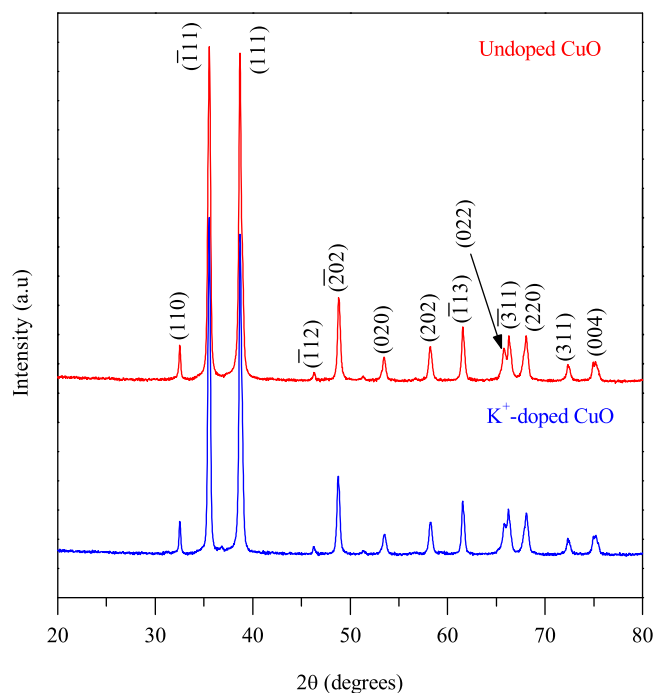

Fig. 1. Powder X-ray diffraction patterns of undoped CuO and K^+-doped CuO samples.

rollers in order to improve the contact between the active material and copper foil. The electrolyte used was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethylcarbonate (1:1 in volume ratio). 2032 coin-type cells were assembled in a glove box under a dry argon atmosphere using lithium metal as a reference electrode, and a polymer membrane together with glass fiber as a separator. The coin cells were kept in the glove box for 12 h for aging before electrochemical measurements. The cyclic voltammogram (CV) test was carried out on both the samples at a scan rate of 0.1 mV s^{-1} in the potential range of 0.0–3.0 V (vs. Li/Li$^+$) using a Bio Logic Science Instrument (VSP 1075). Galvanostatic testing (BTS–2004H, Nagano, Japan) was used to investigate the electrochemical performance over the potential range of 0.01–3.0 V vs. Li$^+$/Li at different current rates. Electrochemical impedance spectroscopy (EIS) measurements were also carried out on a Bio Logic Science Instrument (VSP 1075) to measure the electronic conductivities of the assembled cells. Before the measurement, the cells were cycled for three cycles and then measured at frequency ranging from 0.01 Hz to 1.0 MHz. A small AC signal of 5 mV amplitude was used for perturbation of the system throughout the tests.

Results and discussion

Crystal structure and morphology

The crystal structure and purities of the obtained undoped CuO and K^+-doped CuO products were analyzed through XRD patterns. Fig. 1 shows the XRD patterns of undoped CuO and K^+-doped CuO samples. All peaks of both the XRD patterns shown in Fig. 1 can be clearly assigned to the standard monoclinic structure of CuO (JCPDS file no. 05-0661, *C2/c*), and there are no additional peaks of K impurities, implying that the K-doping did not change the original CuO structure. Therefore, it could be also suggested that the K^+ ions are highly dispersed in the matrix of the CuO [16]. In addition, the lattice constants were also calculated using the least square refinement method from the unit cell program. The obtained