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Germanium anode with lithiated-copper-oxide nanorods as an electronic-conductor for high-performance lithium-ion batteries

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ABSTRACT

Lithiated-CuO nanorods were used as a nanostructured electronic-conductor of the current-collector for Ge anode to improve the performance of lithium-ion batteries. By limiting the voltage cut-off window in a range which could avoid the discharge–charge plateaus of CuO after the initial discharge, the lithiated-CuO nanorods can act as an electronic-conductor. The obtained Ge anode exhibits an excellent rate capability and superior cyclability. At a current-density of 1 A/g, the anode presents a capacity retention of above 95% even after 100 cycles. The anode also presents a stable rate performance even at a current-density as high as 10 A/g. The enhanced performance can be mainly ascribed to the lithiated-CuO nanorods which could result in a nanocable structure that offers short electron/lithium-ion transport path, enough buffering space for the huge volume change of Ge coating and excellent electrical contact between the Ge coating and the current-collector.

1. Introduction

Thus far, lithium-ion batteries (LIBs) have been the vital power sources for portable electronic devices, electrical vehicles and storage of renewable energy. With the development of the aforementioned applications, LIBs with high-power and high-energy density are urgently desired. It is essential to develop electrode materials with high reversible capacity, long cycle life and high rate capability [1]. Si and Ge are considered as promising candidates for anodes of LIBs because of their high theoretical specific capacities. Compared with Si, Ge attracts less attention since its high cost and lower capacity. However, the electrical conductivity of Ge is 10^4 higher than that of Si and the diffusivity of Li-ion in Ge is 400 times faster than that in Si at room temperature, which makes Ge be a more promising anode for high-power LIBs [2]. Unfortunately, similar to Si, Ge anode undergoes a rapid capacity fading caused by severe volume change during Li-ion insertion and extraction. Fabrication of nanostructured amorphous Ge is seemingly a promising solution to solve the above issue. Although the anodes prepared through directly depositing Ge coating on nanostructured current-collectors always exhibit improved Li storage performance, the nanostructured current-collectors usually cannot avoid using templates or reduction/high-temperature processes, which are commonly complicated and expensive [3,4].

Herein we report a lithiated-CuO nanorods supported Ge anode for LIBs. By limiting the voltage cut-off window in an appropriate range, the CuO nanorods could irreversibly react with Li-ion only in the initial discharge and become a conductive mixture which could act as an electronic-conductor. The areal mass loading and the electrochemical performance of the anode were significantly enhanced by such a strategy.

2. Experimental

The CuO nanorods were fabricated by a galvanostatic-anodization of Cu plate followed by a heat-treatment, as described in our earlier publication [3]. Briefly, the anodization was carried out at a current density of 1.5 mA/cm^2 in a 1 M NaOH aqueous solution at room temperature for 5 min. Then the electrochemical-etched Cu plate was heated at 160 °C in a vacuum for 10 min and cooled down naturally to room temperature. Ge coating was deposited onto the CuO nanorods by using an electron-beam-evaporator. The purity of Ge is 99.9999%. The evaporation was conducted with a deposition rate of 0.2 nm/s under a high vacuum of 10^{-4} Pa. The thickness of the coating was monitored with a quartz thickness sensor. The substrate of the CuO nanorods was heated to 150 °C and steadily rotated over the evaporation source for a high homogeneity of Ge coating. The contrast sample was prepared on planar Cu plate under the same deposition condition.

The morphologies of the samples were characterized by a Hitachi S-4800 field-emission scanning electron microscope

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(SEM). Raman spectra were obtained by a Jobin-Yvon Horiba HR800 spectrometer with a 532 nm-wavelength excitation. X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max-IIIC X-ray diffract meter using Cu K_α radiation (0.15406 nm). The active mass of Ge was obtained by measuring the mass difference before and after deposition via a Mettler XS105 analytical balance. The mean mass loading of Ge is 0.36 mg/cm^2.

Coin-type half-cells were assembled using the obtained electrode as an anode. The electrolyte was 1 M lithium hexafluorophosphate dissolved in ethylene carbonate and dimethyl carbonate (1: 1 by vol.). The galvanostatic discharge-charge cycling was tested in the voltage range from 0.02 to 0.7 V.

3. Results and discussion

Fig. 1a shows XRD patterns of the as-prepared $Cu(OH)_2$ and CuO nanorods, which are consistent with the data of JCPDS 13-0420 and JCPDS 05-0661, respectively. It indicates that the product of the anodization of Cu plate is $Cu(OH)_2$, and $Cu(OH)_2$ is totally turned to CuO after a heat-treatment. From Raman spectra shown in Fig. 1b, it can be seen that the Raman signal of CuO is disappeared after Ge deposition, which indicates that the Ge coating is relatively thick. The Raman-shift of the Ge coating is located at 170 and 270 cm^{-1}, which means that the Ge coating is amorphous. The amorphous Ge coating is benefit to a faster insertion/extraction of Li-ions and a stable cyclability because the diffusivity of Li-ions in amorphous material is much higher than that in crystalline one, and the volume change is homogeneous and leads to less pulverization for amorphous structure [5].

Fig. 2a shows that the diameter of the $Cu(OH)_2$ nanorods is 100–200 nm, and the straight nanorods are crosslinked. Fig. 2b shows the SEM image of the CuO nanorods. It can be seen that the panoramic three-dimensional structure of the $Cu(OH)_2$ nanorods still remains after a 180 °C heat-treatment in a vacuum. The insets in Fig. 2a and b indicate that, after the heat-treatment, the obtained CuO nanorods become curve, but the diameter is not apparently changed comparing with the $Cu(OH)_2$ nanorods. Fig. 2c shows that, although the CuO nanorods are fully covered with Ge, the three-dimensional structure is still maintained. Based on the insets in Fig. 2b and c, the thickness of the Ge coating was estimated to be about 150 nm. As shown in Fig. 2d, Ge is conformal coated on each CuO nanorod and the coating is quite even. The insets in Fig. 2d show that the shadow effect is not obvious in such a deposition configuration and the nanorods are partially interconnected.

Fig. 3a shows the first two discharge-charge voltage profiles of the obtained Ge anode. It is noted that the capacity in the first discharge is above 3500 mA h/g and the discharge plateaus above 0.7 V are consistent with those of CuO [6]. Thus, the ultra-high capacity can be ascribed to the reduction of CuO, which only appears in the first discharge process in the present experimental configuration. It can be seen that the characteristic voltage plateaus of CuO are disappeared as soon as the voltage cut-off window was set as 0.02–0.7 V after the first discharge. The discharge-charge plateaus after the first discharge are belong to Ge. The reactions for the CuO nanorods in the first discharge are irreversible, and the formed composite nanorods of Cu and Li_2O are conductive, which could act as an electronic-conductor [7].

Cyclability of the electrodes with current-densities of 1 A/g and 2 A/g (the initial three cycles were performed with a current density of 50 mA/g) is illustrated in Fig. 3b. An anode of the Ge film on planar Cu plate was cycled at 1 A/g as contrast. It can be seen that the capacity of the contrast anode drops dramatically in the first few cycles and delivers a capacity of only 130 mA h/g after 100 cycles. In comparison, the lithiated-CuO nanorods supported Ge anode is able to operate at higher current-densities and delivers a superior cyclability. At a rate of 1 A/g, the first discharge capacity was 1044 mA h/g, which maintained at 1014 mA h/g after 100 cycles. The first reversible capacity at a rate of 2 A/g was 892 mA h/g, which decreased slowly to 730 mA h/g after 200 cycles.

The rate performance of the Ge anode at the rates from 0.2 to 10 A/g is presented in Fig. 3c. As the rate increasing, it apparently presented a stable rate performance at all the test rates. Notably, the obtained anode delivers a specific capacity of about 650 mA h/g at a rate as high as 10 A/g. After 11 cycles at 10 A/g, the cycling rate is returned to 200 mA/g and the capacity recovered to 1180 mA h/g. It is noted that such a capacity is kept quite well after the subsequent 50 cycles, which indicates that the obtained Ge electrode is of excellent rate capability and stable structure.

The excellent rate performance and cyclability could be attributed to the unique configuration of the electrode. First, the lithiated-CuO nanorods/Ge coating core-shell structure could provide short Li-ion diffusion path and high conductivity, and largely

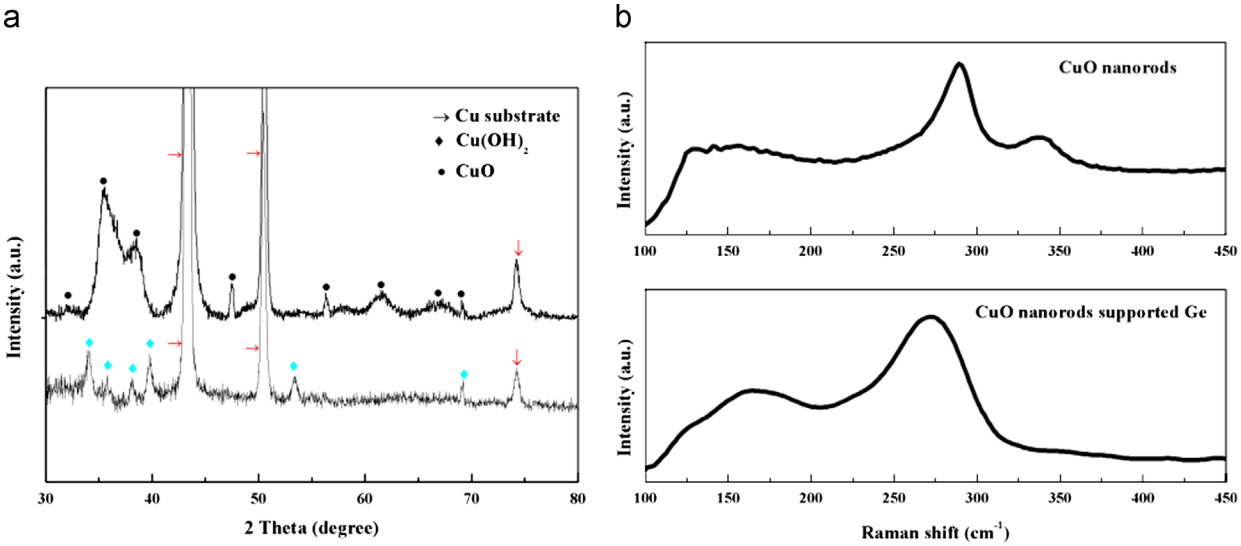

Fig. 1. (a) XRD patterns of the as-prepared $Cu(OH)_2$ and CuO nanorods; (b) Raman spectra of the CuO nanorods and CuO nanorods supported Ge coating.