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Tailoring the morphological properties of anodized Ti_3SiC_2 for better power density of Li-ion microbatteries

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ABSTRACT

In this work, it is reported that the morphology of negative electrodes based on anodized Ti_3SiC_2 has a strong influence on the electrochemical performance of Li-ion microbatteries. Ti_3SiC_2 was anodized in an aqueous electrolyte containing hydrofluoric acid to form an oxide film. Two typical porous structures produced at low and high applied potentials were examined by scanning electron microscopy and characterized by X-ray diffraction, mercury intrusion porosimetry, and electrochemical techniques. The power density delivered by the nanolayered structure obtained at 10 V is almost 3 times higher than that obtained from a mesoporous material formed at 60 V. Cyclic voltammetry has been used to explain that this enhanced electrochemical property is related to the higher amount of Li^+ stored at the surface of the nanolayered structure.

1. Introduction

Li-ion batteries (LIBs) have been widely used as energy storage devices in microelectronics [1–3]. However, the demand for high energy, power capability, low-cost, and safe LIBs drives the research for new electrode and electrolyte materials [4,5]. In recent years, substantial efforts have been made toward the development of nanostructured electrode materials for LIBs because of the superior electrochemical performances [2,6–8]. Recently, we reported on the fabrication and electrochemical performance of a new nanostructured anode material for Li-ion microbatteries (μLIBs) obtained by anodization of a Ti_3SiC_2 MAX phase [9]. We reported that two typical morphologies could be obtained by varying the applied potential; at a low potential (10 V), a nanolayered structure was obtained, while at a high potential (60 V), a mesoporous structure was formed. A mix of the two morphologies was observed at 30 V. MAX phases are a large family of 70 + layered ternary metal carbides and/or nitrides with composition of $M_{n+1}AX_n$: where M is an early transition metal; A is an A-group element; X is carbon and/or nitrogen; and n can be 1, 2, or 3 [10]. The anodized Ti_3SiC_2 (henceforth referred to as A-Ti_3SiC_2) shows promising electrochemical performance [11–13]. In this work, we report that the morphology of anodized Ti_3SiC_2 has a strong influence on the electrochemical performance of LIBs. Actually, the power density delivered by the nanolayered structure is almost 3 times higher than that obtained from the mesoporous material. A detailed electrochemical study has been performed to explain that this enhanced electrochemical property is related to the higher amount of Li^+ stored at the surface of the nanolayered structure.

2. Experimental

A polished and cleaned fully dense Ti_3SiC_2 was electrochemically anodized in aqueous 1 M H_3PO_4 + 1 M NaOH electrolyte containing 0.1% vol. HF for 3 h at applied potentials of 10 V and 60 V. Anodic applied potentials leading to high electrical fields ($>$ 10 V/μm) are required to ensure the migration of oxidized species and achieve the formation of a thick oxide layer. The anatase phase was obtained by annealing the as-formed A-Ti_3SiC_2 at 450 °C in air for 3 h.

The cyclic voltammetry (CV) and galvanostatic charge-discharge tests were performed using two-electrode Swagelok cells. The half-cells were assembled by using the as-formed A-Ti_3SiC_2 film grown on the conducting Ti_3SiC_2 support as the working electrode, and Li foil as a reference electrode. A Whatman glass microfiber paper soaked in 1 M $LiPF_6$ in EC:DEC electrolyte was used as a separator. The galvanostatic charge-discharge tests were performed at 200 μA cm^{-2} in the potential window of 1–3 V vs. Li/Li^+. The CV experiments were carried out at various scan rates (0.05–1.3 mV s^{-1}) in the potential window of 1–3 V vs. Li/Li^+.

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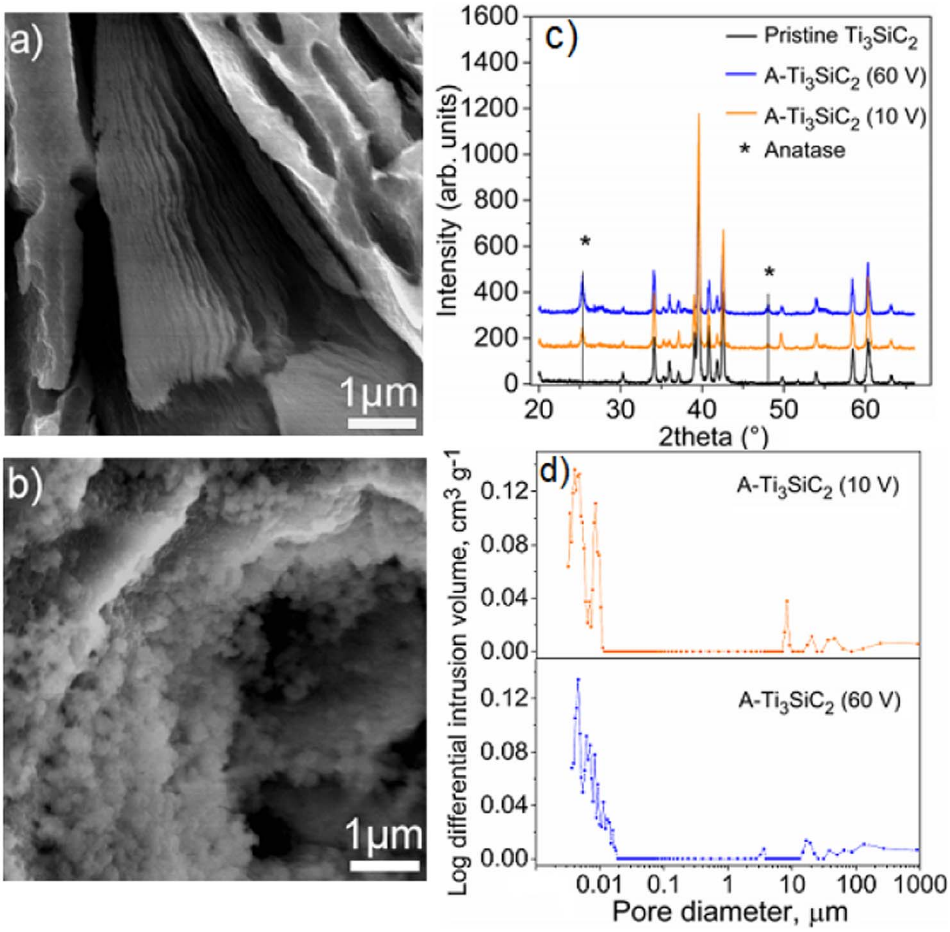

Fig. 1. SEM images of Ti_3SiC_2 anodized in 1 M H_3PO_4 + 1 M NaOH containing 0.1% vol. HF for 3 h at (a) 10 V and (b) 60 V. (c) Corresponding XRD patterns and (d) plots of the log differential intrusion volume as a function of pore diameter.

The morphology of the A-Ti_3SiC_2 was characterized by a field-emission scanning electron microscope (FE-SEM, Philips XL-30 FEG SEM). The structures were investigated by X-ray diffraction (XRD) using a Siemens D5000 diffractometer. Mercury intrusion porosimetry (MIP), Pore Master 60 QuantaChrome, was used to determine the pore size and pore fraction.

3. Results and discussion

The oxide morphology formed after the anodization of Ti_3SiC_2 is governed by the competition between electrochemical oxide formation and chemical dissolution [9]. At the low applied potential, the A-Ti_3SiC_2 _ has adopted a nanolayered structure with a thickness of 3 μm (Fig. 1a), while a porous morphology with a thickness of 21 μm is obtained at the high potential (Fig. 1b). It can be noticed that as Ti is a valve metal, the thickness of the oxide layer increases with the applied potential. Similar anodization conditions were used to fabricate self-standing TiO_2 nanotubes [14].

Fig. 1c shows the XRD patterns for the pristine and anodized at 10 V and 60 V Ti_3SiC_2. The peaks at 25.19° and 48.01° correspond to the (101) and (200) reflections of anatase, respectively. The anatase phase has a structure of tetragonal with the space group of $I4_1/amd$ and crystal size of 17 nm (JCPD file no. 21-1272). Fig. 1d shows the plots of the log differential intrusion volume as a function of pore diameter. A-Ti_3SiC_2 (60 V) has an average pore size of 5 nm with a porosity of ~20%. A-Ti_3SiC_2 (10 V) reveals 11 nm and 4 nm pores and total porosity of 35%.

In agreement with previous reports, the two CV curves (Fig. 2a and b) exhibit well-defined cathodic and anodic peaks at 1.67 and 2.17 V vs. Li/Li^+, respectively, that correspond to lithium insertion/extraction potentials in anatase. The reversible insertion/extraction of Li^+ process is given by Eq. (1) [15,16].

$$TiO_2 + xLi^+ + xe^- \rightleftharpoons Li_xTiO_2 \tag{1}$$

The mole fraction of inserted lithium (x) into anatase is close to 0.5 and corresponds to a theoretical specific capacity of 168 mAh g^{-1} [15,17]. Higher current densities are obtained for A-Ti_3SiC_2 (60 V) due to the formation of a thicker porous oxide layer during the anodization of Ti_3SiC_2 at applied potential of 60 V. The total charge stored in A-Ti_3SiC_2 is strongly dependent on the scan rate. As shown in Fig. 2, increasing the scan rate results in the increase of peak current values as well as broadening and shifting of peak positions to lower and higher potentials. These electrochemical behavior results from kinetic limitations to the diffusion of Li^+ within titania and the ohmic drop effects [13,18,19].

Fig. 2c shows the first galvanostatic charge-discharge profiles. The insertion/extraction voltage plateaus are consistent with the redox peaks observed in the CVs. The first discharge capacity values are very close, i.e. 24 μAh cm^{-2} $μm^{-1}$ and 22 μAh cm^{-2} $μm^{-1}$ for A-Ti_3SiC_2 (10 V) and A-Ti_3SiC_2 (60 V), respectively. Fig. 2d shows the electrochemical performance of A-Ti_3SiC_2 electrodes performed at the same kinetic for 30 cycles. The capacity loss after the first cycle can be induced by the irreversible reaction of Li^+ with trace water molecules, Li^+ trapping within the structural defects of titania, and the formation of a solid electrolyte interphase (SEI). The last discharge capacity values are 29 μAh cm^{-2} $μm^{-1}$ and 18 μAh cm^{-2} $μm^{-1}$ for A-Ti_3SiC_2 (10 V) and A-Ti_3SiC_2 (60 V), respectively. To compare the electrochemical performance of the two samples at a current density of 200 μA cm^{-2} after 30th cycle, a Ragone plot (Fig. 3e) has been established using data given in Table 1.

Compared to the mesoporous structure, the porous nanolayered morphology delivers a higher power density that can be attributed to