Journal of Electroanalytical Chemistry 791 (2017) 56–63

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Influencing factors of low- and high-temperature behavior of Co-doped Zn_2SnO_4–graphene–carbon nanocomposite as anode material for lithium-ion batteries

Zhenhai Gao [a,b,c], Xiaoting Zhang [a], Hongyu Hu [a,*], Dalei Guo [a], Hui Zhao [b,c], Huili Yu [b,c]

[a] State Key Laboratory of Automobile Simulation and Control, Jilin University, Changchun 130025, PR China
[b] State Key Laboratory of Vehicle NVH and Safety Technology, Changan Automobile Holding Ltd., Chongqing 401120, PR China
[c] Changan Automobile Holding Ltd. Automotive Engineering Institute, Chongqing 401120, PR China

ARTICLE INFO

Article history:
Received 20 January 2017
Received in revised form 6 March 2017
Accepted 10 March 2017
Available online 11 March 2017

Keywords:
Anode
Zn_2SnO_4
Low-temperature performance
High-temperature performance

ABSTRACT

Zn_2SnO_4-based anode materials have recently attracted considerable attention due to their high capacity and low price for lithium-ion batteries. However, their performance is affected by temperature and temperature-dependent characters have not been investigated sufficiently. In this regard, we tested the electrochemistry performance of Co-doped Zn_2SnO_4–graphene–carbon (Co–ZTO–G–C) nanocomposite anode at various temperatures (−25, 25 and 60 °C) and analyzed the main limitations and improvements of its low- and high-temperature behavior. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results demonstrated that severe concentration polarization, the absence of Zn_2SnO_4/Zn(Sn) redox couple and large charge-transfer resistance R_{ct} limited its low-temperature performance. Further electrochemical performance analysis indicated that the doped Co could effectively decrease R_{ct} of the nanocomposite and improve its capacity at low temperature. It also suggested that graphene and carbon layer contributed to maintaining its capacity during high-temperature cycles. Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) results revealed that the performance degeneration of the nanocomposite at elevated temperature was mainly attributed to severe volume expansion/contraction of Zn_2SnO_4 nanoparticles and destruction of Zn_2SnO_4 cubic structure. The XRD results also showed that the cubic structures of Zn_2SnO_4 at all temperatures were destroyed after cycling, which led to cyclic performance degeneration of the Co–ZTO–G–C nanocomposite.

1. Introduction

Owing to its high energy and power density, long life cycle and environmental friendliness [1,2], rechargeable lithium-ion battery (LIB) has been widely employed as energy source for portable supplies. Literatures show that the performance of LIB is sensitive to its operating temperature [3–5]. When working at low (<0 °C) or elevated temperatures (40–80 °C), LIB may not perform very well. Temperature has been long considered as a popular research interest, because it is related to the performance, lifespan and safety of LIB [6]. At low temperature, especially under −20 °C, the energy and power densities of LIB decrease significantly, which is mainly caused by the large charge-transfer resistance at electrode-electrolyte interface, and the limited lithium ion diffusion in the electrode, electrolyte and the solid-electrolyte-interphase (SEI) film [7,8]. In addition, the lithiation process is typically more difficult than the delithiation process in the anode at low temperature, which results in the formation of lithium dendrites on the anode electrode surface. The formed lithium dendrites will lead to the subsequent growth of the SEI film and even cause safety issues [9]. At elevated temperature, electrode materials degenerate increasingly, and the electrolyte decomposition and undesirable electrolyte-electrode interfacial reaction are accelerated greatly [6]. These factors would decrease the capacity, shorten battery life and even provoke the onset of thermal runaway [10]. In short, the low- and high-temperature performance of LIBs greatly depends on anode materials [9,11,12]. Therefore, anode electrode materials should be the focus of the research on widening the operating temperature range of LIBs.

As the conventional anode material, graphite suffers from low capacity, limited rate performance and poor safety at temperatures below −20 °C and above 50 °C [10,13,14]. On one hand, various methods have been used to improve the electrochemistry performance of graphite at low and elevated temperatures, such as mild oxidation [15], metal doping [16], design and assembly of electrode [7] and coating [17]. On the other hand, plenty of studies attempted to look for alternative anode materials with high cyclic capacity and rate capability for Li-ion batteries [18–23]. Among them, the temperature-dependent characters of carbon [6], $Li_4Ti_5O_{12}$ [24,25], Li_3VO_4 [26] and the oxides (TiO_2, SiO)

---

[*] Corresponding author.
E-mail address: huhongyu@jlu.edu.cn (H. Hu).

http://dx.doi.org/10.1016/j.jelechem.2017.03.020
1572-6657/

[10,13,27] have been reported. However, the reports about the performance of zinc tin oxide anodes at low and elevated temperatures are few. Zinc stannate (Zn_2SnO_4) is a promising candidate anode, owing to its excellent high theoretical capacity (1231 mAh g^{-1}), high electrical conductivity and low price [28,29]. But it is well known that the large volume changes restrict its application. To improve its performance, Zn_2SnO_4 is combined with carbonaceous to increase its conductivity and reduce its volume expansion during alloying/dealloying process [30,31]. Doping is another strategy to enhance its electrochemical performance by improving the conductivity of electron and ion in the Zn_2SnO_4 nanoparticles [32,33]. Recently, our group has prepared the Co-doped Zn_2SnO_4–graphene–carbon (Co–ZTO–G–C) nanocomposite through a facile one-step hydrothermal method. The reversible capacity of the hybrid was up to 699 mAh g^{-1} at 0.1 C after 50 cycles. The formed carbon layer and graphene subtract acted as the carbonaceous media. Co was a dopant. Although the electrochemical performance of the Co–ZTO–G–C nanocomposite at normal temperature has been investigated [33], its performance analyses at low and elevated temperatures are still valuable.

In this study, we analyzed the factors affecting the electrochemistry performance of Co–ZTO–G–C nanocomposite anode for LIBs at −25, 25 and 60 °C. The L^+ intercalation/deintercalation mechanism of Co–ZTO–G–C nanocomposite at all temperatures was firstly obtained by cyclic voltammetry (CV). Furthermore, the effects of each component of Co–ZTO–G–C nanocomposite, such as the doped Co, graphene and carbon layer, on its cyclic durability and electrochemical impedance were investigated to understand the contribution of each component to its electrochemistry performance at various temperatures. Finally, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and X-ray diffractometer (XRD) were employed to analyze the surface composition, morphology and crystal structure of the Co–ZTO–G–C nanocomposite electrodes after cycles, respectively. This was for further understanding the degradation mechanism of its electrochemistry performance at various temperatures.

2. Experimental

2.1. Sample synthesis

The synthesis of sample was according to a previous report [33]. All of the reagents used in our experiments were analytically pure. In a typical fabrication, 5 ml of ethylene glycol mixed with 15 ml of 1.8 mg ml^{-1} graphene oxide aqueous suspension was used as a solvent. 1.5 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$ with 0.3 mmol $Co(CH_3COO)_2 \cdot 4H_2O$ and 1.5 mmol $Na_2SnO_3 \cdot 3H_2O$ were separately dissolved into the above mixed solvents. Subsequently, the two solutions were mixed uniformly by vigorous stirring. Afterward, ammonia solution was added into the hybrid to adjust its pH to around 9, which was followed by adding 1 mmol L-ascorbic acid. After stirring, the mixed liquor was transferred into a Teflon-lined autoclave and heated at 180 °C for 12 h. After cooling down to the room temperature, the precipitate was collected by centrifugation, washed with deionized water and ethanol for three times, and dried at 60 °C. The final products were obtained by heat treatment at 450 °C for 3 h in N_2 atmosphere and denoted as Co–ZTO–G–C. With the same synthesis procedure of the Co–ZTO–G–C, the composites prepared without adding $Co(CH_3COO)_2 \cdot 4H_2O$ were named ZTO–G–C; those prepared without adding ammonia solution and L-ascorbic acid were named Co–ZTO–G; and those prepared without graphene oxide were named Co–ZTO–C. In addition, commercial graphite (99.8%, Alfa Aesar Chemical Co. Ltd., China) was used as a reference.

2.2. Electrochemical measurements

CR2025 half-coin cells were used. For the preparation of the working electrode, active materials, acetylene black (AB) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10 were homogeneously dispersed in *N*-methyl-2-pyrrolidone. The mixture was loaded onto a Cu foil uniformly. After drying in vacuum at 60 °C, Cu foil was cut into wafer (6 mm in diameter) as working electrode. The cells were assembled in an argon-filled glove box with 1 M $LiPF_6$ in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 vol.) as electrolyte, Celgard 2300 as separator, and Li foil as counter and reference electrodes. In this electrochemical test, the weight of active material on the electrode was about 1.0 mg.

The galvanostatic charge/discharge and rate performances were recorded on Land battery measurement instrument (LAND CT2001A, Wuhan Jinno Electronics Ltd., China) in a potential range of 0.01–3 V (vs. Li^+/Li) at −25, 25 and 60 °C. The cyclic voltammetry (CV) and Electrochemical impedance spectra (EIS) were performed on a CHI650D electrochemical workstation (Shanghai Chenhua Instruments Ltd., China) at −25, 25 and 60 °C. The measured cells in CV and EIS were fresh without cycling.

2.3. Material characterizations

The surface composition and oxidation state of the electrodes were characterized by X-ray photo-electron spectrometry (XPS) recorded on an ESCALAB 250 spectrometer. The morphologies of electrode surface were observed by a field emission scanning electron microscope (FESEM, JSM-6700F, Japan). The crystalline phases of the anode after cycles were tested by X-ray diffractometer (XRD, DMax/2500P, Rigaku, Japan) utilizing Cu Kα radiation ($\lambda = 1.5406$ Å). Samples of XPS, SEM and XRD for investigations were prepared by dismounting the cell in the glove box, subsequently cleaning the anode electrode with dimethyl carbonate, and drying it in air. The measured cells were in charged (delithiated) state.

The synthesis and structure characterization of Co–ZTO–G–C nanocomposite have been reported by our group [33]. The ultrafine (3–5 nm) Co-doped Zn_2SnO_4 nanoparticles showed cubic structure with a space group Fd3m. The carbon layer was formed from the carbonization of L-ascorbic acid during the hydrothermal process. The graphene nanosheets were crumpled and embedded in the composite. In Co–ZTO–G–C nanocomposite, the total weight percentage of carbon, including carbon layer and graphene nanosheets, was about 12.5%. The integral morphologies of Co–ZTO–G–C nanocomposite pristine electrode, which was composed of Co–ZTO–G–C nanocomposite, AB and PVDF, are shown in Fig. 1.

3. Results and discussion

Fig. 2a, b and c show the charge/discharge curves of Co–ZTO–G–C nanocomposite obtained at 0.1C in the potential range of 0.01–3.0 V at −25, 25 and 60 °C respectively. The nanocomposite delivered initial discharge and charge specific capacities of 625 and 196 mAh g^{-1} at −25 °C, 1395 and 870 mAh g^{-1} at 25 °C, and 1552 and 965 mAh g^{-1} at 60 °C, respectively. After the first cycle, its capacity at −25 °C retained 23% of that operating at the room temperature. At the same current density, the capacity of commercial graphite after the first cycle at −20 °C was only 12% of that at 20 °C [34]. At 25 and 60 °C, the first discharge specific capacities of the nanocomposite exceeded the theoretical capacity of Zn_2SnO_4 (1231 mAh g^{-1}), which might be caused by the formation of SEI layer, the insertion of lithium ions into graphene, carbon layer and acetylene black, and interfacial storage [35]. Apparently, its initial discharge and charge specific capacities increased with the increasing temperature. Fig. 2d displays the coulombic efficiency of Co–ZTO–G–C nanocomposite at various temperatures. The initial coulomb efficiencies of the nanocomposite were 31%, 62% and 61% at −25, 25 and 60 °C, respectively. Its initial coulomb efficiency at −25 °C was only half of that at 25 °C. Its initial coulombic efficiency at 60 °C was equivalent to that at 25 °C, indicating that elevated temperature did not greatly increase the irreversible reaction between the Co–ZTO–G–C nanocomposite electrode and electrolyte. From the second cycle, its