The critical effect of electrodes components mixing on efficiency of anode material for lithium-ion batteries

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ABSTRACT

An investigation is attempted to highlight the importance of electrode preparation. Graphite carbon (GC), SnO2 and single wall carbon nanotubes (SWCNT) were used as components of anode catalyst for lithium-ion batteries. For mixing these materials, two common processes were performed: ball milling of GC + SnO2 + SWCNT and dispersion of SWCNT in GC-SnO2. The composite electrode prepared from dispersion step presented a superior performance, due the formation of porous and hollow microstructure, which provides more lithium storage sites, shorter Li⁺ diffusion length and sufficient void space.

1. Introduction

Lithium ion batteries (LIB) have achieved great market share since their commercialization by Sony in 1990 [1,2]. Carbon graphite (CG) is currently the commercial anode material, but it presents a low theoretical capacity (372 mA h g⁻¹), encouraging the use of others forms of carbon materials such as graphene, nanofibers, and carbon nanotubes [3–7]. In order to create cooperative effect metal oxides-carbon composites, SnO2 has been considered a promising candidate for high energy density LiBs [8–12].

However, it is known that in addition to the appropriate materials, it is necessary that the interaction between the components takes place [6,13]. Especially for electrochemical responses such as stability, reversibility and kinetics of Li insertion/extraction process, an attempt is made for further understanding of how component mixing of solid ingredients affects the electrochemical performance of single wall carbon nanotubes (SWCNT) on C-SnO2 composite electrode. To emphasize the importance of this issue, this letter illustrates how the electrode preparation method can affect the anode electrode performance for LIB.

2. Experimental section

Commercialized SWCNT (Carbon Nanotechnologies Inc.®, carbon > 95%, lot P0323, specific surface area (SSA): 380 m² g⁻¹), CG (Sigma-Aldrich®) and SnO2 (Nanostructured & Amorphous Inc.®, SSA: 5.5 m² g⁻¹) were used as raw material, without further purification to prepare the final products. CG-SnO2 and CG-SnO2-SWCNT composites were mixing at the weight ratios 1:1 and 1:1:1, respectively, and were ball-milled using a planetary ball (Fristen GmbH) in a stainless-steel vessel under Ar atmosphere at a speed of 140 rpm for 6 h. The ball-to-powder weight ratio was 20/1. The composite was synthesized by a simple two step-process: first, CG-SnO2 was ball-milled at the ratio 1:1 following the same procedure previously mentioned. Then, CG-SnO2-SWCNT at a weight ratio of 1:1:1 were sonicated in toluene solution (Aldrich®) for 1 h by a probe sonicator. The previously prepared CG-SnO2-SWCNT product was then collected by filtration and dried in a vacuum oven at 100 °C for 12 h. The obtained product was denoted as [CG-SnO2]-dSWCNT.

The electrochemical measurements were conducted by assembly into coin cells. The working electrodes were prepared by mixing the active material, acetylene black and PVDF (Aldrich®) at a weight ratio 80:10:10, respectively, and 0.25 cm² of area. Lithium foil was used as a counter electrode. A polypropylene microporous film was used as separator. LiPF₆ (1 mol L⁻¹) in ethylene carbonate and dimethyl carbonate (1:1, v/v, Merck) was utilized as an electrolyte. Cyclic voltammetry (CV) measurements were conducted on a CH660A electrochemical analyzer. The cells were cycled at a current density of 10 mA g⁻¹ in a voltage 2.00-0.01 V using a computer-controlled charger system manufactured by Neware Battery Testers. Electrochemical impedance spectroscopy (EIS) was performed by using an Ametek PARSTAT® 2273 electrochemistry workstation, with 10 mV amplitude and in 100 kHz – 10 mHz of frequency range.

3. Results and discussion

Morphologies of the CG-SnO2-SWCNT and [CG-SnO2]-dSWCNT are
shown in Fig. 1. Due to the simple mixing of composites, there was no chemical reaction between them. However, CG-SnO2-SWCNT (Fig. 1 (a)) is an example of the possibility of seeing ball-milled materials as an agglomerate from all materials indicated being composites. On the insert, it is possible to observe only few particles of SnO2 mixing with the graphite and the SWCNT, indicate a poor iteration between them. On the other hand, Fig. 1 (b) shows a better distribution of oxide particles, and the adherence of SnO2 on the SWCNT and on CG. Consequently, the structure shows many irregular hollow supporting carbons. The main mechanism of ultrasonic is the cavitation bubbles formation at low pressures [14]. The propagation of ultrasound can result at mechanical, acoustic cavitation, heating and chemical effects. At a heterogeneous solid-liquid reaction, ultrasonic treatment can uniform mixing of reactants, and controls their particle size and distribution [15,16]. It is then expected that [CG-SnO2]-SWCNT may be able to promote adsorption of electrolytes into the electrode and enhance the transportation of Li\(^+\) over the entire electrode.

Fig. 2 (a), (b) and (c) shows cyclic CV curves at scan rate 0.1 mV s\(^{-1}\) for CG-SnO2, CG-SnO2-SWCNT and [CG-SnO2]-dSWCNT, respectively. The first Li\(^+\) intercalation curve was hardly different from the subsequent ones for both composites. There is no well-defined peak. Moreover, this is a multistep electrochemical process, including the formation of a solid electrolyte interphase (SEI) layer on the electrode, irreversible reduction of SnO2 to metal Sn, reversible formation of Li\(_x\)Sn alloys (0.0 ≤ x ≤ 4.4) and insertion of Li\(^+\) in the carbonaceous material [12,17–21]. After the initial cycle, there is a cathodic peak at 0.90 V and it can be assigned to the formation of Li\(_x\)Sn alloys. During discharge process, anodic peaks are observed at 0.60 and 1.30 V, corresponding to the decomposition of Li\(_x\)Sn alloys and lithium de-insertion from vacancies in ball-milled graphite, respectively [22].

The charge-discharge profiles of composite electrodes are presented in Fig. 2 (d)-(f). The first charge and discharge capacities are 753 and 392 mAh g\(^{-1}\) for CG-SnO2, 1009 and 277 mAh g\(^{-1}\) for CG-SnO2-SWCNT and 2921 and 735 mAh g\(^{-1}\) for [CG-SnO2]-dSWCNT. The initial efficiencies of these samples are 52%, 27% and 25%, respectively. The results demonstrate that SWCNT contribute to the larger initial irreversible capacity. This behavior is due to reduction of surfaced functional groups, formation of SEI and, the large amorphous carbon content [23].

Fig. 3 presents the EIS measurements for the different electrodes. Nyquist plot are shown for the freshly assembled cells (Fig. 3 (a)) and subsequently after cycled 20 times. For both systems, the equivalent circuit was the same, represented at Fig. 3 (c). Rs is described as electrolyte solution resistance. R\(_t\) and C\(_p\) are associated with Li-ion migration resistance and pseudo-capacitance, respectively [19,24]. R\(_{CT}\) and C\(_{CT}\) refer to the charge-transfer process, and Z\(_w\) is associated the Li-ion diffusion [19]. The simulation results showed at Table 1 illustrated that after 20 cycles the charge transfer resistance (R\(_{CT}\)) decreased. Probably the electrolyte accessibility improved by cycling the material [25]. The charge/discharge process leads the composite to balance the stress of the CG-SWCNT-SnO2 interconnected network and the volumetric expansion of SnO2 during cycling. The association of the surface area and pores is beneficial to facilitate the rapid diffusion of Li\(^+\) to access the SnO2 [26]. However, after 20 cycles the R\(_{CT}\) for C-SnO2-SWCNT and [C-SnO2]-dSWCNT were smaller compared to the C-SnO2 sample. This indicates that the electronic conductivity improved due to the good electrical conductivity of SWCNT in the composite materials, where they served as both an active material and a conductor in the anode composite [27].

Fig. 4 (a) compares the cyclic performance of CG-SnO2, CG-SnO2-SWCNT and [CG-SnO2]-dSWCNT electrodes. Comparatively, an obvious improvement can be observed in cyclability with [CG-SnO2]-dSWCNT electrode, which achieves a reversible capacity of 377 mAh g\(^{-1}\) after 30 cycles, while the reversible capacities of CG-SnO2, CG-SnO2-SWCNT electrodes are 191 mAh g\(^{-1}\) and 280 mAh g\(^{-1}\), respectively. The influence of SWCNT considering the effect of components mixed into C-SnO2 composites are shown in Fig. 4 (b). The calculated SWCNT contribution is obtained from Eq. (1):

\[
C_{CSWCNT} = \frac{C_{C-SnO2-SWCNT} - C_{C-SnO2}}{X_{SWCNT}}
\]

where C\(_{CSWCNT}\), C\(_{C-SnO2-SWCNT}\), C\(_{C-SnO2}\) is the specific capacity of contribution of SWCNT, the specific capacity of CG-SnO2-SWCNT or [CG-SnO2]-dSWCNT and CG-SnO2 is obtained in this work, respectively. X\(_{SWCNT}\) weighs a fraction of SWCNT in the CG-SnO2-SWCNT or (CG-
SnO$_2$-dSWCNT composite materials. It can be seen that the dispersing mode of SWCNT has great influence on the cycle performance of the composite when it is compared with graphite carbon. By contrast, when all components of CG-SnO$_2$-SWCNT were ball milled, SWCNT lead to contribution lower than graphite carbon. This data shows that Li$_{1.7}$C$_6$ and Li$_{0.64}$C$_6$ alloys were formed at the 30th cycle for [CG-SnO$_2$]-dSWCNT and CG-SnO$_2$-SWCNT, respectively (Fig. 4 (b)). The higher rate capability of [CG-SnO$_2$]-dSWCNT than CG-SnO$_2$-SWCNT can be explained as follows: i) ball milling process agglomerated the tubes with CG-SnO$_2$ reducing the lithium diffusion; ii) SWCNT dispersion favored a porous structure, which produces a diminution path Li$^+$. The improved performance for dispersed SWCNT is due to the unique porous structure, as seen at Fig. 1(b).

4. Conclusion
It was notable that the performance of composite content CG, SnO$_2$ and SWCNT as anode material for lithium-ion batteries are affected as the products are mixed. The mode of electrode preparation can modify the surface morphology and, consequently, the affinity between the particles and the Li$^+$, which is beneficial to improve the cyclic stability of composite electrode. Additionally, the introduction of SWCNT in C-SnO$_2$ composites facilitate not only possess good cyclability during charge-discharge, which would facilitate the electron transport, but also offers a large surface area which made for enhancing the capacity. When SWCNT are dispersed, the porous structure is responsible for the excellent electrochemical performance. This opens another way to improve the performance of the battery and to work out a series of further study.

Declaration of Competing Interest
None.

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