Preparation, characterization, and electrochemical performance of Li$_2$CuSnO$_4$ and Li$_2$CuSnSiO$_6$ electrodes for lithium batteries

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**Abstract**

Lithium copper tin silicon oxide was prepared from their precursor compounds using Brij surfactant and different sources of Si such as SiO$_2$, SiC, and Si$_3$N$_4$. A hydrothermal autoclave method was used in the first stage of the preparation. X-ray diffraction characterization revealed that the crystal structures of these compounds were tetragonal. Scanning electron microscope investigation showed that the particle size morphology of Li$_2$CuSnSiO$_6$ is larger than that of Li$_2$CuSnO$_4$. Electrochemical impedance spectroscopy explained that the cell prepared from the Li$_2$CuSnSiO$_6$ electrode using Si$_3$N$_4$ precursor had a lower charge-transfer resistance (38 $\Omega$) than that of Li$_2$CuSnO$_4$ ($R_{ct} = 2936 \Omega$). Furthermore, the reversible specific discharge capacity of the Li$_2$CuSnSiO$_6$ cell was 870 mAh/g in comparison with 780 mAh/g for the Li$_2$CuSnO$_4$ cell after 100 cycles.

**Keywords**

Preparation, Characterization, Electrochemical, Performance, Li$_2$CuSnO$_4$, Li$_2$CuSnSiO$_6$, Electrodes, for, Lithium, Batteries

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Preparation, Characterization, and Electrochemical Performance of Li2CuSnO4 and Li2CuSnSiO6 Electrodes for Lithium Batteries

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Rechargeable lithium batteries have been considered an attractive power source for a wide variety of applications in popular electronic devices such as mobile telephones, video tape recorders, and laptop computers. Nowadays, these batteries are being scaled-up for prospective use in electric vehicles and energy storage. Therefore, the development of lithium batteries into advanced utilities is considered an important goal to meet a great demand. Different types of active materials have been investigated for both positive and negative electrodes.1–8

To develop high capacity anode for lithium-ion batteries, silicon and some metals that can alloy with lithium at a high molar ratio are being exploited and developed as promising anode materials.9–11

Tin-based oxides have attracted much attention, as they have been considered as a potential substitute for the current graphite electrode (theoretical capacity 372 mAh g−1), primarily on the basis of their higher theoretical reversible specific capacity (e.g., 781 mAh g−1 for SnO2).1,2

When SnO2 was used as the anode material of lithium-ion batteries, tin works as the virtual part, and its reversible capacity is based on the formation and decomposition of lithium tin alloys, LiSn, Li2Sn3, Li3Sn2, Li4Sn3, Li5Sn2, or Li2Sn.2,3 The practical application of SnO2, however, is hampered by poor material cyclability arising from the large specific volume change (300%) in repetitive charging and discharging of the battery, which causes mechanical failure and the loss of electrical contact at the anode.3,5 SnO2 undergoes severe phase changes during the lithiation and delithiation processes with severe volume expansion and contraction.

Thin films of a few nanostructured carbon-free anode materials (SnO2, Li2O–SnO2, CuO–SnO2, and Li2O–CuO–SnO2 composite) were prepared. Li2O was introduced to suppress the aggregation of the Li–Sn alloy; CuO was introduced to combine more Li per Sn metal and to improve the discharge capacity by enlarging the voltage range. These novel composites display outstanding cyclability.2,3 SnO2 undergoes severe phase changes during the lithiation and delithiation processes with severe volume expansion and contraction.

Fine powders of tin oxide doped with traces of silicon in combination with highly dispersed amorphous silicon oxide have been synthesized by an advanced flame-assisted ultrasonic spray pyrolysis method.7 Upon addition with enough Si, the irreversible reaction capacity, as well as the oxidation state of Sn, reduces significantly.11 When the silicon content in the precursor was high enough, some metallic tin appeared in the product. Huang et al. indicated that the addition of some Si(OMe)4 to the precursor will reduce the oxygen content of the final product. Because the oxygen bound to Sn is responsible for the observed irreversible capacity, a low oxidation state is highly beneficial for this anode material.7 Furthermore, a reversible capacity of 900–950 mAh g−1 was found for these composites. This improved performance was explained due to an enhanced interfacial diffusion caused by highly dispersed inert second phases, i.e., SiO2 and LiSi4O6.

We can also see that the introduction of SiO2 into the Li1−xO–Cu1−xSnO4 system will improve the specific capacity through the intercalation and deintercalation of Li with Si. This study is an attempt to study the electrochemical performance of this quaternary metal oxide system (Li1−xO–Cu1−xSnO4–SiO2). Also, the amount of reported literature on this system is small, and more data are needed.

Experimental

Materials preparation.— Stoichiometric amounts of CH3COOLi (Alfa Aesar), (CH3CO2)2Cu (Aldrich), and stannous oxalate (Aldrich) were dissolved separately in distilled water to prepare Li2CuSnO4. Brønsted 30 % CH3OH/C2H5OH/OCH3CH2OH/H2O surfactant was added in a weight ratio of 5:1 wt/wt with respect to the active materials. To prepare Li2CuSnSiO6, we used Si3N4 (Nanostructured and Amorphous Materials Inc., US, 15 nm), SiC (MTI Corporation, ≤30 nm) and SiO2, fumed silica 5 nm, CABOT GmbH). The raw material compounds were then mixed together. The mixed solution was stirred and heat-treated at 80°C for 2 h. The mixture was then transferred to an autoclave vessel (250 cm3) and heat-treated at 250°C for 10 h. Finally, the samples were calcined in air atmosphere at 750°C for 12 h in an alumina crucible. The samples were left to cool down to room temperature inside the furnace. The samples were sintered again for another 12 h at the same temperature in air.

Materials characterizations.— Powder X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer with Cu Kα radiation. IR absorption spectra were recorded using an FT/IR-6300 type-A Fourier transform infrared (FTIR) interferometer. Samples were ground to fine powders, mixed, and diluted with KBr. The IR region examined was 400–4000 cm−1. Elemental compositions of the various tin oxide compounds were...
analyzed by inductively coupled plasma (ICP, Perkin-Elmer Optima 2000 DV). Scanning electron microscopy (SEM) was conducted with a JEOL SEM model 6460.

Electrochemical measurements.— The homogeneous slurry used to form the electrodes was composed of 85 wt % active materials, 10 wt % acetylene black, and 5 wt % poly(vinylidene fluoride) binder dissolved in N-methyl pyrrolidone solvent. It was then spread onto Cu foil substrates. The area of each coated electrode was 1 cm². The electrodes were dried in a vacuum oven under a vacuum pressure of 30 Torr at 110°C for 12 h. The electrodes were then pressed at a pressure of 2000 kg/cm². The active material loading was about 4 mg for each individual electrode. CR2032 coin cells were then assembled in an argon-filled glove box (Mbraun, Unilab, Germany), using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume, provided by Merck). The cells were galvanostatically charged and discharged over a voltage range of 0.0–3 V vs Li/Li⁺ electrode.

Results and Discussion

Structural characterization.— XRD patterns of the Li₂CuSnO₄ and Li₂CuSnSiO₆ samples showed suitable crystallinity as shown in Fig. 1. The samples’ diffraction peaks exhibited good crystalline structures. Their structures were indexed to the tetragonal system using Rietveld analysis of the XRD pattern data with a standard software package. The refined unit cell parameters are given in Table I. The crystallite sizes of Li₂SnCuO₄ and Li₂CuSnSiO₆ prepared from different sources of Si: (2) SiC, (3) Si₃N₄, and (4) SiO₂.

Table I. Unit cell parameters of tetragonal Li₂CuSnO₄ and Li₂CuSnSiO₆ samples.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Samples</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Cell volume, V (Å³)</th>
<th>Selected 2θ (°)</th>
<th>fwhm (°)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li₂CuSnO₄</td>
<td>4.752</td>
<td>3.203</td>
<td>72.3285</td>
<td>34.55</td>
<td>0.778</td>
<td>11.1836</td>
</tr>
<tr>
<td>2</td>
<td>Li₂CuSnO₄/SiC</td>
<td>4.841</td>
<td>3.294</td>
<td>77.1958</td>
<td>34.1</td>
<td>0.289</td>
<td>24.3040</td>
</tr>
<tr>
<td>3</td>
<td>Li₂CuSnO₄/Si₃N₄</td>
<td>4.913</td>
<td>3.375</td>
<td>81.4643</td>
<td>34</td>
<td>0.308</td>
<td>28.2495</td>
</tr>
<tr>
<td>4</td>
<td>Li₂CuSnO₄/SiO₂</td>
<td>4.795</td>
<td>3.254</td>
<td>78.8160</td>
<td>34.1</td>
<td>0.5</td>
<td>17.4017</td>
</tr>
</tbody>
</table>

L = 0.94λ/ω cos θ

where θ and ω are the Bragg angle and the full width at half-maximum (fwhm) peak, measured in radians, of each diffraction peak, respectively. Also, λ is the X-ray wavelength (1.54056 Å) and L is the effective particle or grain size. It is observed that the unit cell parameters of Li₂SnCuSiO₆ are greater in value than those of Li₂SnCuO₄.

Figure 2 shows an SEM image of the samples. The powders have average crystal sizes of 50 and 100 nm. In general, the particles have an interconnected network structure in the form of nanoaggregates.

Electrochemical measurements.— Electrochemical impedance spectroscopy (EIS) may be considered as one of the most sensitive tools for the study of differences in electrode behavior due to surface modification. The electrochemical impedance spectra of the cells, as presented in Fig. 4, show an intercept at high frequency on the real axis Z’ for the resistance of the electrolyte, Rₑ, followed by a semicircle in the high-middle frequency region and a straight line in the low frequency region. The numerical value of the diameter of the semicircle on the Zreal axis is approximately equal to the charge-transfer resistance, Rct, and therefore, it can be seen that there is a marked decrease in Rct after the addition of the silicon compound. The straight line in the low frequency region is attributed to the diffusion of the lithium ions into the bulk of the electrode material, or the so-called Warburg diffusion. The plot of the real part of the impedance, Z’, vs the reciprocal root square of the lower angular frequencies is displayed in Fig. 5. The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode material.
or the so-called Warburg diffusion. This relation is governed by Eq. 2. It is observed that the Warburg impedance coefficient, $\sigma_{\text{w}}$, is 652.82 $\Omega \cdot s^{0.5}$ for the Li$_2$SnCuSiO$_6$ cell, and it has a lower value than in Li$_2$SnCuO$_4$ (1415.839 $\Omega \cdot s^{0.5}$). The parameters of the equivalent circuit are presented in Table II. Also, the diffusion coefficient values of the lithium ions for diffusion into the bulk electrode materials have been calculated using Eq. 3 and are recorded in Table II.

$$Z_{\text{ct}} = R_e + R_{\text{ct}} + \sigma_w \cdot \omega^{-0.5}$$  \hspace{1cm} \text{[2]}

$$D = 0.5(RT/\pi F^2 \sigma_w C)^2$$ \hspace{1cm} \text{[3]}

$$Z_{\text{ct}} = R_e + R_{\text{ct}} + 2\sigma_w \cdot C_{\text{dl}}$$ \hspace{1cm} \text{[4]}

The double layer capacitance is given by

$$\omega = 1/(R_{\text{ct}} \cdot C_{\text{dl}})$$ \hspace{1cm} \text{[5]}

where $R_{\text{ct}}$ is the charge-transfer resistance, $R_e$ is the electrolyte resistance, $\omega$ is the angular frequency in the low frequency region, $D$ is the diffusion coefficient, $R$ is the gas constant, $T$ is the absolute temperature, $F$ is Faraday’s constant, $A$ is the area of the electrode surface, and $C$ is the molar concentration of Li$^+$ ions.\textsuperscript{14} The obtained diffusion coefficient ($8.31 \times 10^{-14}$ cm$^2$ s$^{-1}$) for the Li$_2$SnCuSiO$_6$ cell “3” prepared from the Si$_3$N$_4$ precursor explains the higher mobility for Li$^+$ ion diffusion than in the other cell, which lacked Si. Furthermore, the exchange current density is given by the following formula

$$i' = RT/nF \sigma_{\text{ct}}$$ \hspace{1cm} \text{[6]}

where $n$ is the number of electron involved in the electrochemical reaction. Li$_2$SnCuSiO$_6$ cell (b) is higher than for the other cell. Therefore, the charge-transfer reaction of the Li$_2$SnCuSiO$_6$ electrode prepared from Si$_3$N$_4$ is stronger than in the other electrode prepared for the Li$_2$SnCuO$_4$ cell “1”. It is observed that $C_{\text{dl}}$ of cell “3” also has a higher value: 1.95 $\times 10^{-5}$ F.

Cyclic voltammetry measurements were carried out between 0 and 3 V as shown in Fig. 6. The cyclic voltammograms of the investigated samples show a cathodic reduction in the range of 0.51–0.63 V. This peak is attributed to the intercalation of lithium into tin to form Li$_4$Sn compound ($1 \leq x \leq 4.4$) as observed in the reported papers.\textsuperscript{15,16} As we have Li$_2$SnCuO$_4$ and Li$_2$SnCuSiO$_6$ as the starting materials, therefore the reduced forms are Li$_2$SnCu and Li$_2$SnCuSi compounds and their intercalation with Li$^+$ are as follows\textsuperscript{15,16}

$$\text{Li}_2\text{SnCu} + (2.4 - x)\text{Li}^+ + 4e^- \rightarrow \text{Li}_{4.4-x}\text{Sn} + \text{Cu}$$ \hspace{1cm} \text{[7]}

$$\text{Li}_2\text{SnCuSi} + (2.4 - x)\text{Li}^+ + 4e^- \rightarrow \text{Li}_{4.4-x}\text{Sn} + \text{Cu} + \text{Si}$$ \hspace{1cm} \text{[8]}

$$\text{Si} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Si}$$ \hspace{1cm} \text{[9]}

Li$_2$SnCuO$_4$ shows three anodic oxidation peaks at 0.42, 0.85, and 1.7 V, respectively, for the following reactions\textsuperscript{5,7,15,16}

$$\text{Li}_{4.4-x}\text{Sn} + \text{Cu} \rightarrow \text{Li}_2\text{SnCu} + (2.4 - x)\text{Li}^+ + 2e^- \quad E = 0.42 \text{ V}$$

$$\text{Li}_2\text{SnCu} + 1.5 \text{ O}_2 \rightarrow \text{Li}_2\text{SnCuO}_3 + 2e^- \quad E = 0.85 \text{ V}$$

**Table II.** Electrochemical impedance parameters of Li$_2$CuSnO$_4$ and Li$_2$CuSnSiO$_6$ cell samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples</th>
<th>$R_e$ ((\Omega))</th>
<th>$R_{\text{ct}}$ ((\Omega))</th>
<th>$\sigma$ ((\Omega \cdot s^{0.5}))</th>
<th>$D$ (cm$^2$ s$^{-1}$)</th>
<th>$C_{\text{dl}}$ ((\text{F/cm}^2))</th>
<th>$i'$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$_2$CuSnO$_4$</td>
<td>730</td>
<td>2936</td>
<td>1415.83</td>
<td>1.77 $\times$ 10^{-14}</td>
<td>7.77 $\times$ 10^{-7}</td>
<td>7.00 $\times$ 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>Li$_2$CuSnO$_4$/SiC</td>
<td>90</td>
<td>725</td>
<td>801.06</td>
<td>5.52 $\times$ 10^{-14}</td>
<td>8.54 $\times$ 10^{-6}</td>
<td>3.54 $\times$ 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>Li$_2$CuSnO$_4$/Si$_3$N$_4$</td>
<td>22</td>
<td>38</td>
<td>652.82</td>
<td>8.31 $\times$ 10^{-14}</td>
<td>1.95 $\times$ 10^{-5}</td>
<td>6.75 $\times$ 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>Li$_2$CuSnO$_4$/SiO$_2$</td>
<td>146</td>
<td>100</td>
<td>808.252</td>
<td>5.42 $\times$ 10^{-14}</td>
<td>1.09 $\times$ 10^{-6}</td>
<td>2.57 $\times$ 10^{-4}</td>
</tr>
</tbody>
</table>

**Figure 3.** (Color online) FTIR spectra of the prepared Li$_2$SnCuO$_4$ and Li$_2$SnCuSiO$_6$ prepared from Si$_3$N$_4$.  

**Figure 4.** (Color online) EIS spectroscopy of (1) Li$_2$CuSnO$_4$ and Li$_2$SnCuSiO$_6$ from (2) SiC, (3) Si$_3$N$_4$, and (4) SiO$_2$ cells.

**Figure 5.** (Color online) Relationship between real impedance with the low frequencies for (1) Li$_2$CuSnO$_4$ and Li$_2$CuSnSiO$_6$ from (2) SiC, (3) Si$_3$N$_4$, and (4) SiO$_2$.  

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Li$_2$SnCuO$_3$ + 0.5 O$_2$ → Li$_2$SnCuO$_4$ + 2e $\quad E = 1.7$ V

Li$_2$SnCuSiO$_4$, prepared from Si$_3$N$_4$, shows three anodic oxidation peaks at 0.68, 1.05, and 1.85 V for the deintercalation of Li$^+$ from Li$_{4.4-}$Sn, and the oxidation of Li$_2$SnCuSi to Li$_2$SnCuSiO$_4$ and Li$_2$SnCuSiO$_6$, respectively. It is observed that there is a shift in the anodic peaks to more positive potentials. This can be attributed to the change of Si to Si$^{2+}$ and Si$^{4+}$.

The first discharge capacity plateaus vs the working voltage between 3 and 0.0 V are shown in Fig. 7. The profiles for the first reduction look fairly similar for all the samples. There is a plateau that falls in the range between 1.5 and 1.7 V vs Li$^+$ for the reduction of Sn$^{2+}$ to metallic Sn(0). The first discharge curve of cell “3” delivers the highest specific discharge capacity of about 1300 mAh g$^{-1}$. Similar results have been observed in the literature in spite of using different methods of preparation.

Also, the charge–discharge profile for the followed cycles for cell “3” is recorded in Fig. 8. The second discharge voltage started from 2 V; furthermore, the 100th discharge one began at 1.8 V. The drop in voltage from $-3$ to $-1.5$ V was observed in a different literature.

The cycling performance of these cells, as shown in Fig. 9, remained good for 100 cycles with a gradual decrease. The specific discharge capacity of the Li$_2$SnCuSiO$_6$ cell prepared from Si$_3$N$_4$ is about
900 mAh g$^{-1}$ and it is higher than that of the other cells. The higher capacity of the quaternary oxide can be explained on the concept of using mixed types of metal oxide. They can react reversibly with a larger amount of lithium and exhibit improved electrode performance compared to single oxides, and therefore provide benefits from maintaining the structural stability, leading to a good cycling performance.

Conclusions

The addition of Si to Li$_2$SnCuO$_4$ compound improves the electric conductivity as the charge-transfer resistance of Si compounds decreased. The specific discharge capacity of the cell prepared from Li$_2$SnCuSi$_6$ was improved by $\sim$10% in comparison with one prepared from the Li$_2$SnCuO$_4$ compound.

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