Beneficial effects of Mo on the electrochemical properties of tin as an anode material for lithium batteries

A. Fernández a, F. Martín b, J. Morales a, J.R. Ramos-Barrado b, L. Sánchez a, *

a Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Campus de Rabanales, Edificio Marie Curie, Universidad de Córdoba, 14071 Córdoba, Spain

b Laboratorio de Materiales y Superficies (Unidad asociada al CSIC), Facultad de Ciencias, Campus de Teatinos, Universidad de Málaga, Málaga, Spain

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Abstract

A simple, novel method for improving the electrochemical response of Sn in lithium cells is proposed that involves preparing Sn by a reduction procedure in the presence of Mo powders. Four different Mo_xSn_{1-x} mixtures (0 < x < 0.26) were electrochemically tested and their structural and textural properties determined by using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical properties of the resulting composites in lithium cells were studied by galvanostatic, step potential electrochemical spectroscopy (SPES) and electrochemical impedance spectroscopy (EIS) measurements. The mixtures were found to consist of crystalline Sn and Mo; however, the presence of the latter element modified the Sn habit in two ways, namely, by significantly decreasing particle size and increasing the reactivity towards oxygen. Although Mo is inert towards lithium, it increased both the discharge capacity and the capacity retention of the electrode in relation to pure Sn. The improved interparticle connectivity, reduced electrolyte decomposition and decreased charge-transfer resistance observed in the Mo-containing samples appear to be beneficial effects of the addition of Mo.

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1. Introduction

Tin-based compounds have been extensively explored in recent years as alternative negative electrode materials to the traditional choice (graphite) in the search for higher energy Li-ion batteries. Research in this context has focused on the reaction of tin with lithium [1], which forms various Li_xSn reversible alloys with a theoretical capacity as high as 993 Ah kg^{-1}. However, two key issues hindering their commercialization remain unsolved. One is related with the capacity loss observed when starting from tin oxides: the reaction SnO_x + 2xLi^+ → Sn + xLi_2O is irreversible [2]. The other is the inadequate capacity retention of lithium alloys that results from the large volume changes occurring during the formation of different Li-Sn phases. The formation of Li_xSn alloys involves up to five different crystallographic phases spanning the range 0 < x < 4.4 and volume changes as large as 260% [3]. The coexisting phases, with variable Li concentrations, cause inhomogeneous volume expansions that result in anode cracking or pulverization and lead to a loss of electrical contact or poor conductivity that detracts from long-term cycling performance [4].

Volume changes during Li insertion/extraction can be controlled in various ways. The methods most widely used for this purpose involve active materials of small particle size [5,6], the use of intermetallic alloys and/or composite host materials instead of pure metal [7,8], and that of anodes bonded by conductive polymer or a carbon matrix [9,10]. In general, the incorporation of tin particles into an inactive matrix with a view to hindering Li-Sn phase transitions is an effective method. However, the electrodes thus obtained exhibit capacity values lower than those of pure Sn. In general, the Sn content in carbonaceous materials (e.g. C_{0.8}Sn_{0.2} [11], C_{0.42}Sn_{0.58} [12], C_{0.2}Sn_{0.8} [13]) or M_xSn_{1-x} alloys (e.g. Cu_{0.6}Sn [14], Sn_xFe_{0.4}Fe_{0.6}C [15], Mg_{0.2}Sn [16], Ni_{0.2}Sn_{0.8} [17]) does not exceed 50%.

In this context, it would be of interest to develop effective procedures for controlling the Sn/inactive matrix ratio in order to increase the Sn content in the end product as much as possible. In this work we used a scarcely explored approach involving the
dispersion of Sn particles between metallic particles which are inactive to the electrochemical process and useful to improve the electrical conductivity of the active material [18,19]. The metal used should to be inert towards lithium. In this way, one can obtain a high electrical conductivity of the active material [18,19]. The metal dispersion of Sn particles between metallic particles which are active can be altered, in unavoidable capacity owing to the irreversible uptake of lithium to a zero valence state of the elements. In this work, we used a different strategy to exploit the favorable effect of Mo and avoid such a restriction; thus, the element was added during the formation of Sn via a reductive pathway. The electrochemical response of the Sn electrode was thus clearly enhanced.

2. Experimental

All chemicals were analytical grade. Sn was prepared by reducing SnCl4 · 5H2O aqueous solution with KBH4 in the presence of Mo powder. A large excess of KBH4 solution, which was adjusted to pH 12 with 6 M KOH, was employed. The reaction was carried out under continuous stirring to ensure homogenization of the emulsion. The product was collected by centrifugation, washed with distilled water and ethanol, and dried at 150 ◦C in 1 h under vacuum.

Chemical analyses of the samples were performed by atomic absorption spectroscopy (AAS) and energy-dispersive X-ray analysis (EDX). X-ray powder diffraction (XRD) patterns were recorded in steps of 0.02◦ and 1.2 s on a Siemens D5000 X-ray diffractometer, using Cu Kα radiation and a graphite monochromator. Scanning electron microscopy (SEM) images were obtained on a Jeol JMS-6400 microscope. X-ray photoelectron spectra were recorded on a Physical Electronics PHI 5700 spectrometer using non-monochromated Mg Kα radiation (hv = 1253.6 eV) and a hemispherical analyser operating at constant pass energy of 29.35 eV. The samples were prepared as pellets 7 mm in diameter. High resolution spectra were recorded at 45◦ takeoff angle by a concentric hemispherical energy electron analyser operating in the constant pass energy mode at 29.35 eV, using a 720 m-2 diameter analysis area. The multiregion spectra were recorded in three different areas separated by 1 mm. The energy scale of the spectrometer was calibrated by using the Cu 2p3/2, Ag 3d5/2 and Au 4f7/2 photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. Binding energies were corrected by using that for C 1s of adventitious carbon (and the methyl group) fixed at 284.8 eV.

3. Results and discussion

Four MoSnx−1 mixtures named A–D of compositions over the range 0 ≤ x ≤ 0.26 (where x is referred to atomic values) were studied. Their XRD patterns (Fig. 1) were indexed on the Sn or Mo structure. No peaks belonging to SnO2 and/or MoO2 phases were observed. The unit cell dimensions and crystallite size of Sn – the latter of which was determined from the Scherrer equation [22] – are shown in Table 1 together with the mixture composition as determined by chemical analysis. The presence of Mo had little effect on the structural parameters of Sn obtained except for a slight decrease in crystallite size that was less marked for sample C. The two phases apparent and the absence of changes in the lattice parameters rule out the formation of Mo–Sn solid solutions.

Judging from the SEM images (Fig. 2), the presence of Mo altered the morphology of the tin particles. Thus, sample A consisted of particles of ill-defined shape that were 1–3 μm in size. Mo was present as round particles and the Sn particles tended to form agglomerates around the Mo particles. Moreover, the presence of Mo strongly decreased the size of Sn particles to a few tenths of a micron. A uniform distribution of both types of metallic particles was inferred from the EDX results.
The XPS spectra for the samples are shown in Figs. 3 and 4. The Sn 3d<sub>5/2,3/2</sub> doublet for sample A (Fig. 3a) was split into two components, which suggest the presence of two different oxidation states of Sn at surface level [23,24]. The low-energy component was assigned to Sn and the high-energy component to a SnO<sub>x</sub> layer coating the particles. Sputtering with Ar<sup>+</sup>-ion decreased the intensity of this component and increased that of the low-energy component. The XPS concentration depth profiles for tin and oxygen, Fig. 3b, reveal the disappearance of oxygen after 6 min of sputtering. On the assumption of a depth 6 nm per min of ion Ar<sup>+</sup> etching, a thickness of 36 nm was estimated for the SnO<sub>x</sub> layer, equivalent to 1.2–3% of the particle volume. Such a small amount of SnO<sub>x</sub> phase was undetectable in the corresponding XRD patterns. Because the estimated thickness was greater than the penetration depth of the X-ray beam, the observation of two types of Sn (unoxidized and oxidized) raises some doubts concerning the actual surface composition of the particles. A model based on the Sn particles uniformly coated by a SnO<sub>x</sub> layer of the above thickness would be inconsistent with the XPS data. These are better interpreted by assuming either the Sn particles to be non-uniformly coated by the oxidized phase or the presence of a fraction of unoxidized particles.

The Sn 3d spectra for the mixtures were similar profile to those described above (Fig. 4a); however, the intensity of the high-energy component was now greater than that of the low-energy component. This suggests an increased oxygen content in the Mo-containing samples by virtue of their decreased particle size (45 versus 25% of the oxygen present in pure Sn). The Mo 3d signal-to-noise ratio was very low and increased with etching.

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Table 1

<table>
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<tr>
<th>Sample</th>
<th>Composition</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>L (Å) 200</th>
<th>L (Å) 101</th>
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<td>A</td>
<td>Sn</td>
<td>5.836 (2)</td>
<td>3.185 (2)</td>
<td>18.587</td>
<td>940</td>
<td>964</td>
<td></td>
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<tr>
<td>B</td>
<td>Mo&lt;sub&gt;0.12&lt;/sub&gt;Sn&lt;sub&gt;0.88&lt;/sub&gt;</td>
<td>5.830 (2)</td>
<td>3.185 (3)</td>
<td>18.568</td>
<td>808</td>
<td>826</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Mo&lt;sub&gt;0.17&lt;/sub&gt;Sn&lt;sub&gt;0.83&lt;/sub&gt;</td>
<td>5.826 (4)</td>
<td>3.175 (5)</td>
<td>18.497</td>
<td>920</td>
<td>923</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Mo&lt;sub&gt;0.26&lt;/sub&gt;Sn&lt;sub&gt;0.74&lt;/sub&gt;</td>
<td>5.828 (3)</td>
<td>3.181 (4)</td>
<td>18.538</td>
<td>801</td>
<td>859</td>
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</table>

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Fig. 2. SEM images of sample A (a) and C (b).

Fig. 3. (a) Sn 3d XPS spectra obtained for sample A after (-- -- ) 1 min and (---) 5 min of argon etching. (b) Variation of the Sn and O atomic percentages as a function of the Ar<sup>+</sup> ion sputtering time.
Fig. 4. (a) Sn 3d XPS and (b) Mo 3d spectra obtained for sample D after (—) 1 and (- - -) 16 min of argon etching. (c) Variation of the Sn, Mo and O atomic percentages as a function of the Ar+ ion sputtering time. (Fig. 4b). Also, its binding energy decreased with etching, which suggests that most part of the oxygen is bound to Sn as the Mo 3d doublet was rather symmetric (Fig. 4b). On grounds similar to those used above, the thickness of the SnO coating layer must exceed 240 nm, which is greater than the Sn particle size. The presence of a small amount of uniformly dispersed amorphous SnO may be used as an alternative model to account for the presence of such residual oxygen and is consistent with the XRD patterns, where no traces of crystalline tin oxides were detected.

The electrochemical response of the samples was measured in Li/LiPF₆ EC-DEC/MoₓSn₁₋ₓ cells. The open circuit potential of the cell was about 2.5 V a typical value for metallic Sn versus Li. An abrupt potential drop was observed during the first discharge (Fig. 5) that was followed by a potential plateau at 1.4–1.6 V the length of which decreased with increasing presence of Mo. In fact, no plateau was observed for sample D. The plateau was previously observed by other groups [25–27] and has been ascribed to severely irreversible decomposition of the electrolyte catalyzed by crystal faces of pure Sn [25]. This process only takes place at high potentials (1.5 V versus Li), where the Sn electrode will contain negligible amounts of lithium. The electrolyte decomposes until a thick layer is formed that blocks the catalytic process and hinders further decomposition. Under these conditions, the presence of Mo reduces the extent of this reaction, which does not occur above an atomic content x ≈ 0.26. The resulting reduced particle size and also reduced crystal face size, together with the increased thickness of the oxygen layer coating the crystal faces, may be the origin of this effect. Between 1 and 0.0 V, the potential decrease is smoother and occurs in several steps that correspond to the formation of various LiₓSn alloys [28]. In some reports [29], a plateau at around 0.9 V has been assigned to the reaction of SnO with Li. Although such a reaction cannot be discarded in our samples, the fact that the plateau width was hardly altered by the presence of Mo – which is in contrast with the increased oxygen content found – supports the formation of an alloy. Based on XRD patterns not shown here, Mo is inert towards lithium; therefore, the Faradaic yield of Fig. 5 is referred to the amount of Sn. The amount of lithium inserted below 1 V ranged from 2.8 for pure Sn to 3.2–3.4 for Mo-containing samples (these values are referred to one Sn atom). Therefore, the presence of Mo increases the reactivity of Sn towards lithium, probably as a result of the combined effects of (i) a decreased particle size and (ii) improved Li diffusion resulting from inhibition of the formation of a decomposed electrolyte layer. The presence of Mo also improved the reversibility of the Li reaction, as reflected in the first charge values in Fig. 5 recorded to a cut-off voltage of 1 V. In the Mo-containing samples, the amount of Li removed was greater than that measured for pure Sn (2.8 versus 1.8 Li atoms per Sn atom).

The beneficial effect of Mo was also observed on further cycling. Fig. 6 shows the variation of the specific capacity as referred to the total weight of the electrode with the number of cycles for the Li/LiPF₆ EC-DEC/MoₓSn₁₋ₓ cells. As can be seen, the presence of Mo clearly improved the reversibility of the electrochemical reaction. Although the four electrodes
tested exhibited a capacity loss on cycling. capacity retention was higher in the Mo-containing samples. This parameter, $R_40$, defined as the ratio between the discharge capacity in the fourth and second cycle, ranged from 0.1 for sample A to 0.4–0.6 in the Mo-containing samples. The capacity delivered by the samples with the highest Mo content tended to level off at ca. 275 Ah kg$^{-1}$ at the cycling tests. Although this value is lower than that exhibited by commercial graphite (372 Ah kg$^{-1}$), the increased density of the Mo$_{x}$Sn$_{1-x}$ resulted in higher volumetric capacities (2215–2143 Ah cm$^{-3}$ versus 840 Ah cm$^{-3}$ for graphite). The capacity delivered by these mixtures is higher than that of Mo$_{1-x}$Sn$_x$ solid solutions of composition 0.02 $< x < 0.5$ prepared as thin films by magnetron sputtering, with a delivered capacity of 120 Ah kg$^{-1}$ [30]. However, when these alloys...
are prepared in nanometric size, they contain a small amount of oxygen (the nominal composition is Mo$_{1-x}$Sn$_x$O$_{0.2}$). These two features lead to a significantly increased capacity (300 Ah kg$^{-1}$). These latter results are consistent with those found in this work and confirm the prominent role played by the particle size and the presence of residual oxygen.

In order to shed additional light on the effect of the presence of Mo on the electrochemical activity of Sn, supplementary data were obtained by combining step potential electrochemical spectroscopy (SPES) with ex situ SEM observations and impedance measurements. Fig. 7 shows the step potential curves for Li/sample A and Li/sample D cells cycled over the 1.0–0.0 V range. The different peaks observed during the reduction and oxidation processes were ascribed to the reversible formation of Li$_x$Sn (0.0 < x < 4.4) alloys of variable stoichiometry that provided intensity and potential values consistent with those reported in literature [31]. The sharpness of the peaks suggests the formation of large clusters of Sn and the presence of two-phase regions that caused the capacity to fade [32]. The decrease in peak intensity on cycling was less marked in the Mo-containing samples (Fig. 7b), which provides evidence of the increased reversibility of the reaction.

Ex situ SEM images were obtained upon the addition or removal of lithium from the Sn (sample A) and Mo$_{0.26}$Sn$_{0.74}$ (sample D) electrodes (Fig. 8). A change in the pristine morphology of the particles was observed when both electrodes were discharged up to 0.0 V (Fig. 8a and b). Li$_x$Sn alloys grow as large mismatched aggregates the size of which is difficult to estimate. Round Mo particles were not so clearly observed as in Fig. 2, which suggests that they were coated by Li$_x$Sn alloy. Small cracks were also observed in the surface (images not shown) that became more apparent as the electrodes were charged up to 1.0 V (Fig. 8c and d) through shrinkage of Li$_x$Sn particles during the extraction of lithium [2]. The expansion/shrinking undergone by the Sn structure during the alloying/dealloying process has been cited as the origin of the rapid capacity loss of this electrode and may also be the origin of the cracks. The dilution effect of the Mo particles may hinder it. Moreover, these cracks decrease electronic conductivity between particles aggregates. One interesting observation from the SEM image of the charged Mo$_{0.26}$Sn$_{0.74}$ electrode was the presence of round particles, assigned to Mo, inside the cracks (Fig. 8d). This might mitigate the conductivity loss at the cracks and reduce the electrode impedance. All these features are bound to improve electrode performance, as illustrated in Fig. 6 for the Mo-containing samples.

This last assumption was confirmed by impedance measurements for Sn (sample A) and Mo$_{0.26}$Sn$_{0.74}$ (sample D) electrodes. Fig. 9a shows the impedance spectra for the electrodes at the fifth cycle and at the charged state (cut-off voltage 1.0 V). The shape of the two spectra is highly similar: a well-defined semicircle in the high-frequency domain followed by an incomplete semicircle that overlaps with a line in the low-frequency region. The spectra are typical of the formation of resistive surface films on electrodes. The high-frequency semicircle has been ascribed to Li migration through surface layers and that in the mid-frequency region to interfacial charge-transfer [29,33–35]. The linear part of the spectra reflects the diffusion of Li$^+$ ions into...
Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_e$</th>
<th>$R_1$</th>
<th>$Q_1 \times 10^{-3}$</th>
<th>$n_1$</th>
<th>$R_2$</th>
<th>$Q_2 \times 10^{-3}$</th>
<th>$n_2$</th>
<th>$Q_3 \times 10^{-3}$</th>
<th>$n_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.7</td>
<td>59.2</td>
<td>5.51</td>
<td>0.67</td>
<td>52.6</td>
<td>7.69</td>
<td>0.65</td>
<td>4.24</td>
<td>0.69</td>
</tr>
<tr>
<td>D</td>
<td>9.3</td>
<td>32.1</td>
<td>8.87</td>
<td>0.66</td>
<td>37.2</td>
<td>7.91</td>
<td>0.66</td>
<td>4.04</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Fig. 9. (a) Impedance spectra for samples A (Sn) and D (Mo$_{0.26}$Sn$_{0.74}$) in the charged state at 1.0 V after the fifth cycle. (b) Equivalent circuit used to fit them.

the bulk particles. Alternative models assign the high-to-medium frequency semicircle to charge-transfer and the mid-frequency semicircle to the incorporation of lithium into the lattice [35]. The equivalent circuit used to fit the impedance spectra is shown in Fig. 9b, where $R$ represents a resistance and $Q$ a constant phase element. The impedance parameters obtained are listed in Table 2. The electrolyte resistance ($R_e$) was similar for both electrodes, but the presence of Mo caused a significant decrease in $R_1$ and $R_2$. These results illustrate the two beneficial effects of Mo, namely: improved interparticle conductivity and reduced electrolyte decomposition and a decreased thickness of the SEI film as a result. Also, they may account for the improved capacity retention of the electrodes made from Mo-containing samples on cycling.

4. Conclusions

The effect of Mo particles on the reaction of lithium in Sn electrodes and the electrochemical behavior were evaluated. A simple chemical reduction procedure was used to obtain Mo$_{x}$Sn$_{1-x}$ mixtures ($0 < x < 0.26$) by reducing tin(IV) chloride in the presence of Mo powder. Metallic Sn and Mo phases were only detected in the XRD patterns for the Mo$_{x}$Sn$_{1-x}$ samples. EDAX mapping data revealed a uniform distribution of both elements in the composite material. The presence of Mo modified the crystal growth rate of Sn and resulted in a markedly decreased particle size. Also, it increased the reactivity of the mixtures towards oxygen as revealed by the XPS concentration depth profile analysis. The effects of Mo on the performance of the Li/LiPF$_6$ EC-DEC/Mo$_{x}$Sn$_{1-x}$ cells can be summarized as follows, (i) avoidance of the irreversible electrolyte decomposition observed as an extended plateau at 1.4–1.6 V in pure Sn; (ii) increased lithium uptake, $y$, by Sn via the reaction $Sn + yLi \leftrightarrow Li_ySn$, which occurs over the 1.0–0.0 V range and hence an increased discharge capacity of the electrode; (iii) increased reversibility of this reaction and hence better capacity retention of the cell. SEM images and impedance spectra for the electrodes shed some light on the origin of the effects of Mo. Thus, this element reduces cell impedance as a result of its increasing the electrical conductivity by filling the cracks between isolated tin aggregates and hinders SEI formation at the beginning of the electrochemical process. This must facilitate diffusion of lithium species in the Sn particles and result in improved cell performance. Thus, the use of Mo particles as an inert additive for Sn electrodes is an attractive choice to enhance their electrochemical behavior as anodes in lithium cells. However, further work is required in order to raise the specific capacity delivered by Mo$_{x}$Sn$_{1-x}$ and other mixtures of metals electrochemically active towards lithium, particularly as regards preparation of well-dispersed systems consisting of nanometric particles.

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References
