Electrochemical Behavior of Electrodeposited Sn Films: Possible Negative Electrode for Na⁺ Rechargeable Batteries

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Abstract: Tin films on copper substrate, obtained by electrodeposition procedure, were structural and electrochemical characterized. In particular to investigate the possibility to use such metal as possible negative electrode in Na⁺ rechargeable batteries, EPS (electrochemical potential spectroscopy) and galvanostatic charge/discharge cycling of the electrodes were investigated, at room temperature in organic electrolyte. Three crystalline and one amorphous phases were identified as well as high discharge capacity (738 mAh/g) was obtained after 4 cycles. Unfortunately material fading, due to the internal stress during sodiation/desodiation process, causes poor cyclability.

Key words: Sodium ion batteries, anode materials, electrodeposited tin, potential spectroscopy.

1. Introduction

Since first commercial production of Li-ion batteries in 1991, Li row material has been highly demanded to power not only portable electronic devices but also EVs and HEVs (electronic and hybrid electric vehicles). This issue has turned Li to a strategic and expensive material [1] which is unfortunately in short supply and it may not meet the industrial needs in the near future. This concern has motivated scientists to develop different battery systems and, recently, among them the Na ion rechargeable batteries, which were initially investigated earlier than Li-ion batteries became commercially available [2-4]. Since Na is one of the most abundant elements in the Earth's crust, Na⁺-ion systems can really become alternative for Li-ion batteries. Considering carbon [5] and Na_x(x = 0.66)Mn_{0.5}Fe_{0.5}O₂ [6] as a possible anode and cathode, respectively, the energy density, calculated according

to only active materials weigh, for such a Na ion battery would be around 275 Wh/kg, which is about 70% of commercially available Li-ion battery, so far. This limitation is mainly due to two factors: The discharge voltage profiles of the mixed oxide which would reduce the operative voltage of the whole system and the lower specific capacity of the hard carbon/Na⁺ system compared to the lithiated graphite. Moreover, the specific power of the battery may be limited by the low discharge kinetic of hard carbon. Similar electrochemical properties of Na and Li show that materials, electrolytes, and cell structures, which have been used in Li-ion batteries, may be suitable for Na ion rechargeable batteries; this has been already proven. Many positive electrodes, constituted of some metal oxides (Na_{0.44}MnO₂ [7], Na_xCoO₂ [8] Na_xMn_{0.5}Fe_{0.5}O₂ [6]), NASICON-type materials (Na₃V₂(PO₄)₃ [9]), olivine phases (NaFePO₄ [10]), and others (NaVPO₄F [11]) were successfully used. On the contrary, even if there are some studies of possible anode materials, a good negative electrode is still one of the fundamental impediments in

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progressing Na-ion batteries; in fact, Na does not intercalate between typical graphitic carbon sheets [12]. Nevertheless, other different materials can be used as negative electrodes, among them the Na-metal alloys showing, in phase diagram, wide biphasic regions can play an important role; in particular, if the composition of each compound has high amount of sodium. For this reason, the Na-Sn system was investigated; in fact, as reported by Sangster and Bale [13], at temperatures lower than 100 °C, many biphasic regions with compounds having large amount of sodium (from NaSn₆ to Na₁₅Sn₄) are present. In such conditions, invariant and high chemical potentials of Na have to be present and electrodes with theoretical capacity of about 850 mAh/g might be realized. However, these capacity values are generally observed for a very few cycles in conventional composite electrodes. Looking at the wide knowledge coming from the investigation of such class of materials in lithium ion batteries, the first source of electrode failure is the decrepitation due to the large volume expansion and contraction during the alloying/dealloying process, respectively. In fact, the commercial available binders are not able to accept the stress induced by the strain coming from the reaction with the consequent electrode pulverization. A good way to avoid using binder is to produce Sn layer directly onto proper current collectors. This can be made by several methods, among them electro-deposition is one of the most convenient procedures for preparing Sn in different morphologies. In addition, this technique is very cheap with respect to the others, and it does not need any advanced facility. For this reason, in the present paper the charge-discharge characteristics of Sn films electrodeposited onto copper current-collectors were performed. The experiments were carried out, at room temperatures, using three electrodes T-shaped Swagelok cells having Na as counter and reference electrode and 1 M NaClO₄ in propylene carbonate as electrolyte; cyclability and capacity of the electrodes were investigated between 0.01 V and 1 V vs. Na/Na⁺ electrode potential.

2. Experiments

2.1 Tin Films Preparation

Tin films have been deposited electrochemically on copper substrates from a chloride bath, using SnCl₂·2H₂O and tri-ammonium citrate [14]. Deposition bath was made of 50 g/L tin chloride(II) and 50 g/L tri-ammonium citrate, dissolved in distilled water. Platinum net, copper foil (1 cm²) and SCE (standard calomel electrode) were used as counter, working and reference electrodes, respectively. Before electro-deposition, copper substrates were degreased in acetone by applying ultrasonic waves. Depositions have been done while solution was stirring, and current density was 24 mA/cm² for all depositions.

2.2 Characterization

Microstructure and chemical composition of Sn metal films have been characterized by SEM (scanning electron microscopy) (Vega TS5136 XM Tescan) equipped with an EDX (energy dispersive x-ray) detector, in high vacuum configuration. X-ray diffraction measurement was carried out by Bruker D8 advance XRD (X-ray diffraction) equipped with secondary beam monochromator, copper source (K α radiation), and operating at 0.02 deg/step, and 3 sec/step.

2.3 Electrochemical Characterization

Electrochemical characterizations were carried out using three electrodes T-shaped Swagelok cells equipped with stainless steel current collectors. Sn films, deposited on Cu substrates, were sandwiched between stainless steel and Na metal disc, the latter pasted on the top of current collector. Metallic Na was used as both counter and reference electrodes, and trilayer polypolypylene membranes were used as separators. Separators were wetted by the solution of 1 M NaClO₄ in propylene carbonate, which was used as electrolyte. In order to remove all the aqueous remains present in the Sn films, all the electro-deposited

samples were dried in vacuum chamber over-night, after drying at 130 °C for 2 h. All potentials are reported vs. Na/Na⁺ electrode value, and the electrochemical characterizations were performed using Biologic VMP3 multi-channel battery tester, at room temperature. Typical Sn load was 2.5 mg/cm².

3. Results and Discussion

3.1 Crystal Structure and Morphology

Fig. 1a shows SEM image of electrodeposited Sn on copper current collector in two different magnifications.

Landscape image and cross section view (Fig. 1b) show very good coverage of Sn on Cu substrate. The Sn tetragonal morphology can be easily observed at higher resolution. The EDX spectra (Figs. 1d and 1e), corresponding to the points a₁ and a₂ in Fig. 1a, show the presence of only elemental tin. In our hypothesis, at the solution/current collector interface a Sn film of few m is firstly formed acting as seeds layer for the growth of highly ordered tetragonal structures. The

total film thickness is about 38 m. It has been proved that such rough morphology shows better cyclic properties with respect to smooth one [15]. Fig. 1c shows the XRD pattern of deposited tin film on copper. There are eight peaks: Six of them can be indexed to tetragonal tin [16], with a lattice parameter of $a = 0.58329(8)$ nm and $c = 0.31826(7)$ nm; the other two peaks can be indexed to the copper current collector.

3.2 Electrochemical Analysis

The Sn film electrodes were assembled into half-cells with Na metal as counter and reference electrodes. No binders or conducting carbon were used. The half-cells were studied using EPS (electrochemical potential spectroscopy) [17], and galvanostatic charge/discharge cycling. In EPS measurement, a series of constant potential steps were applied to the electrochemical cell. On each step, the cell was permitted to attain quasi equilibrium conditions by letting the current decay to a small but

Fig. 1 (a) SEM image of electroplated Sn film at two different magnifications, (b) cross section view of the layer, (c) XRD pattern of Sn and Cu current collector, (d) and (e) EDX spectrums carried out in sites a₁ and a₂, respectively.

finite value ($C/50$, typically ~ 17 mA/g in our measurements). When small voltage steps ($V = 3$ mV in our study) are applied, the charge accumulated on each step can be integrated from the measured current to yield an accurate derivative of the voltage-charge relation. This derivative relationship is a very useful tool to define the evolution of the phase equilibrium inside electrode materials. In fact, under thermodynamic equilibrium condition the potential/composition profile obeys Gibbs phase rule. So, the first derivative of quasi equilibrium charge/voltage curve can show sharp peaks for two-phase regions or bell-like peaks for single-phase regions, revealing whether a phase transformation occurs. Fig. 2a presents potential profiles obtained by EPS for first two cycles of Na-Sn alloying/dealloying between 0.01 V to 1.00 V. It is obvious that alloying/dealloying reaction is not completely reversible as charge-discharge tails are not fit to each others, but a significant amount of capacity (82% and 90% during first and second cycle, respectively) has been recovered. During the first alloying reaction, the capacity was 885 mAh/g, which shows achieving final composition of Na₁₅Sn₄ (theoretical capacity 847 mAh/g).

The larger observed capacity compared to the

expected one may be attribute to the formation of passivating layer on the Sn surface. The first alloying reaction shows a potential profiles, which is different from the others. In fact, three plateaux are observed at 0.160 V, 0.065 V and 0.040 V, which correspond to three very sharp peaks in the differential capacity curve (Fig. 2b). According to the equilibrium phase diagram, it can be assumed that this three peaks correspond to the formation of the NaSn₂, NaSn and Na₁₅Sn₄ phases. This behavior was already observed in Sn micrometric particles [18], showing successive strong irreversible de-alloyings. On the contrary, four different plateaux (labeled 1-4 in Fig. 2) are present in our profiles during de-alloying reaction in both first and the second cycle. These plateaux can be related to the different biphasic regions present in Na-Sn phase diagram [13]. Recently, L. Ellis et al. [19] have reported in situ X-ray measurement for Sn sodiation, and demonstrated the existence of three crystalline and one amorphous phases, corresponding to the four plateaux in the voltage profile, close to this one reported in this work. Accordingly, the equilibrium between Sn/NaSn₃, NaSn₃/NaSn, NaSn/Na₉Sn₄ and Na₉Sn₄/Na₁₄Sn₅ correspond to plateaux 1, 2, 3 and 4, respectively. Fig. 3 shows cycling performance of electroplated tin film at 3 different C-rates. In the

Fig. 2 (a) Galvanostatic sodiation and desodiation curves for the first 2 cycles; (b) same experiment reported as incremental capacity vs. potential.

Fig. 3 Discharge capacity vs. cycle number at three different rates: C/20 (black squares), C/10 (red circles) and C/5 (bleu triangles).

lower rates (C/20 and C/10, corresponding to 42.5 and 85 mA/g, respectively) range, discharge capacity little increases after the first cycle, most likely owing due to improvement of ions diffusion in the solid state.

After the 4th cycle, we have seen decrease in discharge capacity, probably due to active material fading. At higher rate (C/5), the average discharge capacity for the first 6 cycles is 475 mAh/g, which is much less than that at lower rates and highlight that sodiation/desodiation takes place partially. In addition, it seems that C-rate affects directly on the stresses induced by volume expansion/shrinkage taking place during the alloying/dealloying process.

4. Conclusions

We explored the possibility to use tetragonal tin layer, obtained by very cheap method, as electrode in Na⁺-ion rechargeable batteries. The films show very good crystallinity after deposition without any further heat treatments. Alloying/dealloying voltage profiles show similar behavior to that previously reported: Four different bi-phasic regions in the voltage range between 0.01 V and 1.00 V. At low current rates, the specific capacities are in good agreement with the theoretical value of 847 mAh/g, but their values drop after 4 cycles, probably due to active material fading.

At current rate of 170 mA/g (C/5), the specific capacity decreases to 551 mAh/g, but remain more stable for at least 10 cycles. As for similar alloying/dealloying processes (Si-Li System), metal nanostructure thick film could be used to improve cyclability.

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References

- [1] Tarascon, J. M. Is Lithium the New Gold? *Nat. Chem.* **2010**, *10*, 510.
- [2] Tarascon, J. M.; Hull, G. W. Sodium Intercalation into the Layer Oxides Na_xMo₂O₄. *Solid State Ionic* **1986**, *22*, 85-96.
- [3] West, K.; Zachau, C. B.; Jacobsen, T.; Skaarup, S. Sodium Insertion in Vanadium Oxides. *Solid State Ionics* **1988**, *28*, 1128-1131.
- [4] Shacklette, L. W.; Jow, T. R.; Townsend, L. Rechargeable Electrodes from Sodium Cobalt Bronzes. *J. Electrochem Soc.* **1988**, *135*, 2669-2674.
- [5] Stevens, D. A.; Dahn, J. R. High Capacity Anode Materials for Rechargeable Sodium-Ion Batteries. *J. Electrochem Soc.* **2000**, *147*, 1271-1273.
- [6] Mortemard, B. B.; Carlier, D.; Guignard, M.; Delmas, C. Structural and Electrochemical Characterizations of P2 and New O₃-Na_xMn_{1-y}Fe_yO₂ Phases Prepared by Auto-Combustion Synthesis for Na-Ion Batteries. *J. Electrochem. Soc.* **2013**, *160*, A569-A574.
- [7] Sauvage, F.; Laffont, L.; Tarascon, J. M.; Baudrin, E. Study of the Insertion/Deinsertion Mechanism of Sodium into Na_{0.44}MnO₂. *Inorg. Chem.* **2007**, *46*, 3289-3294.
- [8] Berthelot, R.; Carlier, D.; Delmas, C. Electrochemical Investigation of the P2-Na_xCoO₂ Phase Diagram. *Nat. Mater.* **2011**, *10*, 74.
- [9] Saravanan, K.; Mason, C.W.; Rudola, A.; Wong, K. H.; Balaya, P. The First Report on Excellent Cycling Stability and Superior Rate Capability of Na₃V₂(PO₄)₃ for Sodium Ion Batteries. *Adv. Energy Mater* **2013**, *3*(4), 444-450.
- [10] Ellis, B. L.; Makahnouk, W. R. M.; Makimura, Y.;

- Toghill, K.; Nazar, L. F. A Multifunctional 3.5 V Iron-Based Phosphate Cathode for Rechargeable Batteries. *Nat. Mater.* **2007**, *6*, 749-753.
- [11] Barker, J.; Saidi, M. Y.; Swoyer, J. L. A Sodium-Ion Cell Based on the Fluorophosphate Compound NaVPO₄F. *Electrochem. Solid State Letters* **2003**, *6*, A1-A4.
- [12] Slater, M. D.; Kim, D.; Lee, E.; Johnson, C. S. Sodium-Ion Batteries. *Adv. Funct. Mater.* **2012**, *23*, 947-958.
- [13] Sangster, J.; Bale, C. B. The Na-Sn (Sodium-Tin) System. *J. Phase Equilib.* **1998**, *19*, 76-81.
- [14] He, A.; Liu, Q.; Ivey, D. G. Electrodeposition of Tin: A Simple Approach. *J. Mater. Sci. Mater. Electron.* **2008**, *19*, 553-562.
- [15] Shin, N. R.; Kang, Y. M.; Song, M. S.; Kim, D. Y.; Kwon, H. S. Effects of Cu Substrate Morphology and Phase Control on Electrochemical Performance of Sn-Ni Alloys for Li-Ion Battery. *J. Power. Source.* **2009**, *186*, 201-205.
- [16] Swanson, T. *Natl. Bur. Stand.* **1953**, *539*, 24.
- [17] Thompson, A. H. Electrochemical Potential Spectroscopy: A New Electrochemical Measurement. *J. Electrochem. Soc.* **1979**, *126*, 608.
- [18] Datta, M. K.; Epur, R.; Saha, P.; Kadakia, K.; Park, S. K.; Kumta, P. N. Tin and Graphite Based Nanocomposites: Potential Anode for Sodium Ion Batteries. *J. Power Sources* **2013**, *225*, 316-322.
- [19] Ellis, L. D.; Hatchard, T. D.; Obrovac, M. N. Reversible Insertion of Sodium in Tin. *J. Electrochem. Soc.* **2012**, *159*, A1801-1805.