Practical silicon-based composite anodes for lithium-ion batteries: Fundamental and technological features

Nikolay Dimov, Yonggao Xia, Masaki Yoshio *

Department of Applied Chemistry, Saga University, Honjyo 1, Saga City 840-8502, Japan

Abstract

Despite recent worldwide research efforts, composite silicon-based anodes remain at the centre of debate in the field of lithium-ion batteries. Here, we demonstrated that successful development of composite silicon-based anodes requires the simultaneous consideration of two equally important features: fundamental and technological. The fundamental feature dictates that the in situ formed amorphous phase should remain in its amorphous state in order to achieve a long-lasting reversible electrode, while the technological feature implies that the complex active material–binder interactions have to be numerically evaluated in order to tailor the electrode properties in an appropriate way. Only the harmonic consideration of both aspects allows creation of a long-lasting reversible silicon electrode. Examples demonstrating these features are considered and lithium-ion batteries employing hybrid silicon-based electrodes are proposed.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Composite silicon electrode; Lithium-ion batteries; Alloying electrode

1. Introduction

The most promising way to further improve the energy density of lithium-ion batteries is to use new generation anode materials, which have a capacity several times higher than the presently used carbonaceous intercalation hosts. New generation anode materials enable more of the cathode material to be packed into the limited space of the battery interior, thus boosting its energy density close to that of the primary lithium cells. A simple estimation based on the material balance ratio revealed that the highest improvement will be seen if an anode with a capacity as high as $1000\,\mathrm{mAh\,g^{-1}}$ is used instead of a carbonaceous anode [1]. Silicon is the likely candidate due to its unique electrochemical properties, which enable creation of anodes with a practical capacity 2–5 times greater than that of commercially available carbonaceous anodes which have a theoretical capacity of $372\,\mathrm{mAh\,g^{-1}}$, and a practical capacity in the range of 280–$350\,\mathrm{mAh\,g^{-1}}$. However, there has been long-lasting misunderstanding regarding the properties of this type of anodes, thereby hindering their practical development. In the present study, we reveal that there are two equally important fea-

tures of this novel type of anode, fundamental and technological, that should be considered simultaneously during development. Here, we consider both and provide an example of practical lithium-ion battery with a hybrid silicon-based anode.

2. Experimental

A mixture of p-Si ($1\,\mu\mathrm{m}$ particle grain size) and MCMB 6–28 (Osaka Gas Chemical, Japan) at a weight ratio of 1:1 was used as the active material. The ingredients were mixed in a ball-mill (Fritsch, Germany) for 5 h at $250\,\mathrm{min^{-1}}$. The simple active material was chosen on purpose and used in our previous study in order to identify the effect of the important factor interactions on cycle performance of the composite electrode.

Electrode properties were further improved using only the important factors, discovered during our preliminary chemometric investigation [2]. Slurry was prepared in the following manner. Two grams of the active material were mixed with $13.850\,\mathrm{g}$ $1.73\,\mathrm{wt\%}$ aqueous solution of CMC in a ball-mill (Fritsch, Germany) for 3 min at 310 rpm. Weight of the balls was set to $50\,\mathrm{g}$. Then $0.115\,\mathrm{g}$ $40\,\mathrm{wt\%}$ aqueous suspension of SBR (BM-400B, Zeon Co., Japan) used as received by the manufacturer were added and slurry was ball-milled for two more

* Corresponding author. Tel.: +81 952 20 4729; fax: +81 952 20 4729.

minutes at the same rotational speed. Slurry prepared in such a way was homogeneous and exhibited appropriate viscosity. It was then coated on a 20 μm thick copper foil current collector by means of a doctor blade. Drying of the electrodes was performed in an oven under a stream of a fresh hot air at approximately 130 °C. Under these conditions electrodes dried completely in approximately 1.5 min. Dry electrode contained 87.5 wt% active material, 10 wt% CMC, and 2.5 wt% SBR.

For the case of PVdF binder the procedure was essentially the same. Since the PVdF binder contains only one binding component: PVdF, dissolved in *N*-methyl pyrollidone (NMP), mixing was performed in just one stage. Two grams of the active material were mixed with 2.380 g 12 wt% PVdF dissolved in NMP (Kureha Co., Japan) and approximately 3 g NMP in order to form slurry with an appropriate viscosity. The mixture was ball-milled with the same ball-mill and the same balls/active material weight ratio for 5 min at 310 rpm. The rest of the procedure coincides with that for CMC/SBR binder.

Dry electrode prepared with PVdF also contained 87.5 wt% active material and 12.5 wt% PVdF, i.e. both electrodes contained the same relative amounts of binder and active material, which facilitates the direct comparison of these binders. Electrodes were used as prepared, without pressing, because press considerably shortens their life cycle, as discovered in our previous work [2].

Electrodes were tested in both half-cells (versus metallic Li) and lithium-ion cells. As a cathode material for the lithium-ion cell test, we used an Al-doped spinel prepared in our laboratory. It was bound to an aluminum sheet current collector by means of a PVdF-binder (Kureha Co. Ltd.). The positive electrode contained 92 wt% active material, 4 wt% acetylene black (AB) and 4 wt% PVdF. Its practical long-term capacity was found to be 101 mAh g^{-1}, when cycled in a voltage window of 3.2–4.3 V.

3. Method

As mentioned above, silicon has a number of unique electrochemical properties. To the best of our knowledge, layer by layer destruction of the parent silicon phase and amorphous phase formation during electrochemical alloying was observed for the first time by Huang and co-workers [3]. Later works then confirmed that electrochemical alloying leads to direct destruction of the parent silicon crystal lattice and amorphous Li$_x$Si phase formation [4–7]. This electrochemical process is consistent with two coexisting solid states: the pristine Si phase and amorphous Li$_x$Si phase, between which there is a well-defined phase boundary as schematically shown in Fig. 1. The aforementioned mechanism can be observed not only by the decreased intensity of silicon-related peaks in XRD patterns and TEM images, but also by the large polarization between the first and subsequent cycles [7–9]. Hence, the cycling test could not be performed by simply limiting the voltage window as is the case for intercalation hosts, which are expected to show no difference in voltage profiles between the first and subsequent cycles. Therefore, cycling protocols can also be used as a tool for studying this type of electrode.
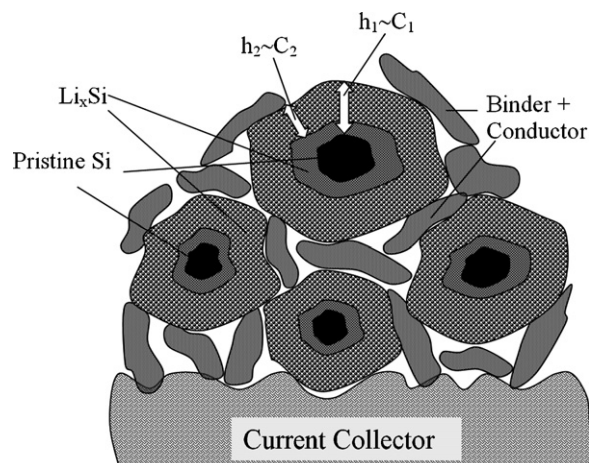

Fig. 1. Sketch of a composite silicon-based anode. Due to the co-existence of pristine silicon (the center of the particle) and amorphous Li$_x$Si alloy (the outer shell of the particle), the capacity of the composite can be expressed by Eq. (1) and as plotted in Fig. 2.

Recently, Obrovac and Krause [10] noted that amorphous alloys have a good life cycle. Therefore, in situ formation of alloys during initial conditioning cycles should, in principle, lead to anodes with high reversibility. Conditioning cycles in this case mean cycling for a couple of cycles at a higher (conditioning) capacity, C_1, and then at a lower (working) capacity, C_2 (i.e. $C_1 > C_2$). The main idea is that conditioning cycles create an amorphous outer shell-like layer on the parent silicon particles. When subsequent cycles are performed at the lower capacity, C_2, the capacity of the outer amorphous layer is sufficient and the phase boundary does not propagate towards the pristine silicon core, which means this structure remains stable over sufficiently long cycle numbers as schematically shown in Fig. 1. However, performing conditional cycles means some of the initially present Li$^+$ from the cathode remains irreversibly bound in the anode, which would reduce much the advantage in higher reversible capacity. From the definition of materials balance ratio it directly follows that percentage of usable capacity from the cathode site would be proportional to the ratio C_2/C_1. Since the advantage of using higher capacity anode can hardly exceed 30% with the currently available materials, either both capacities should be close or coincide (i.e. lack of conditioning cycles), either an extra Li$^+$ source should compensate for the difference $C_1 - C_2$.

The capacity of any silicon-based composite, such as that shown in Fig. 1 is given by the equation:

$$\text{Cap}\,(\text{mAh}\,\text{g}^{-1}) = \frac{x \times 96500 \times 1000}{3600 \times 28.08} \times y \tag{1}$$

where 96,500 C is one Faraday, 1 h contains 3600 s, 1000 is the conversion factor of Ah g^{-1} in mAh g^{-1}, x the mole fraction of Li in Li$_x$Si in the outer particle layer (Fig. 1), and y is the mass fraction of the silicon involved in the electrochemical reaction (the outer amorphous layer of the particles in Fig. 1).

Eq. (1) is graphically presented in Fig. 2. The presence of the multiplier y accounts for the fact that only a fraction of the silicon is involved in the electrochemical reaction and a stable
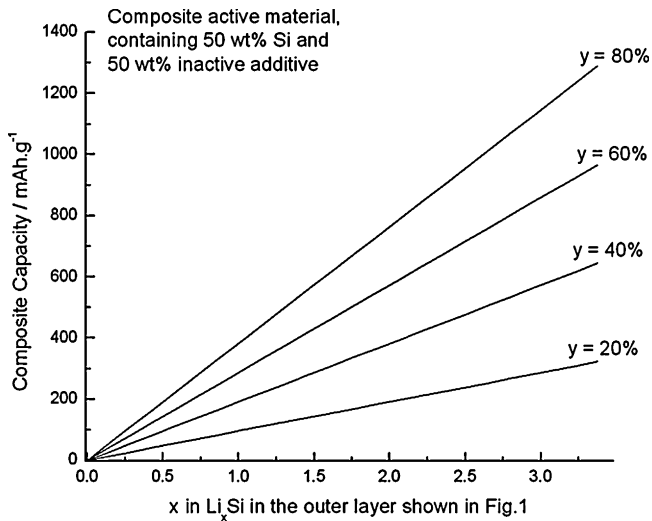
Fig. 2. Si-containing composite capacity as a function of the mole fraction of Li in the Li_xSi alloy (outer layer of the particles in Fig. 1). The various lines show the various silicon mass fractions y, corresponding to various thicknesses h of the amorphous layer, involved in the electrochemical reaction.

electrode structure is more likely if this configuration persists during the cycles. This is a modification of a previously derived expression, which did not take into account this scenario and considered that all available silicon uniformly alloys with Li^+ [9].

Obrovac et al. also revealed that at room temperature and below 50 mV versus Li, the amorphous Li_xSi alloy tends to crystallize giving $Li_{15}Si_4$, which corresponds to 3580 mAh g^{-1}, but not 4200 mAh g^{-1} equivalent to $Li_{4.2}Si$ [10]. Such a capacity limitation was suggested and suspected in our previous study [9], but Obrovac et al. are the first to provide detailed analysis. The above also represents a fundamental feature necessary for understanding silicon-based anodes. As mentioned, "Simply cycling silicon at a fixed voltage or capacity limit from the first cycle onwards leads to the lithiation of new silicon during each successive cycle. Therefore, more silicon is being lithiated in each cycle and eventually all the silicon in such cells will become lithiated, leading to a sudden and severe capacity fade, which has unfortunately led to misleading conclusions in the recent literature [10]".

We believe that the fixed capacity cycling protocol, adopted in our previous studies [2,7–9] help to understand the technological considerations required for developing such anodes. It is important to define the advantage of employing a fixed capacity cycle test protocol and determine why this cycle protocol is a powerful analytical tool, rather than a disadvantage. To do so, let us consider a situation whereby we do not know or understand a priori all complex interactions and physical constants defining the properties of a composite electrode film containing silicon as an active, high-capacity ingredient. Note that in this case it is not even clear which properties of the composite silicon electrode should be taken into account as a basis for improvement. Obviously electrode-processing factors, such as binder type and content, silicon particle size and content, conductive phase type and content, influence the properties of the composite electrode.

However, all these effects are a priori unknown and one has to study them carefully in order to achieve specific information. Despite this seemingly hopeless situation, it is possible to reach a global maxima in the cycle performance/reversibility for a given active material–binder combination just by means of the fixed capacity cycle protocol combined with an appropriate experimental design, in which the coulomb efficiency per cycle is adopted as the main response factor. This simple approach previously revealed the importance of each factor and factor interactions when preparing composite silicon-based electrodes [2]. Actually, as noticed [10], the coulomb efficiency per cycle when using a fixed capacity test protocol represents a direct estimate of the amount of silicon involved in each successive cycle. With this simple information only it is possible to determine the optimum conditions. In addition, it is unnecessary to use any complex instrumental methods, which in many cases lead to misleading data interpretation or do not make sense of the properties of the silicon-based composite electrodes. Thus, the coulomb efficiency per cycle when the capacity is fixed from the first cycle is the net effect of all (known and unknown) factor interactions and a priori unknown parameters. Such information is indispensable, and considered the simplest and most direct way of understanding the technological features of silicon-based anodes.

It is noteworthy to point out that the fixed capacity cycle test should be considered a measure of electrochemical titration, showing in a very direct manner the ability of the electrode to resist deterioration, despite the lack of conditioning cycles and that new silicon is involved in the electrochemical process in each cycle. Note also that this test gives reproducible results,
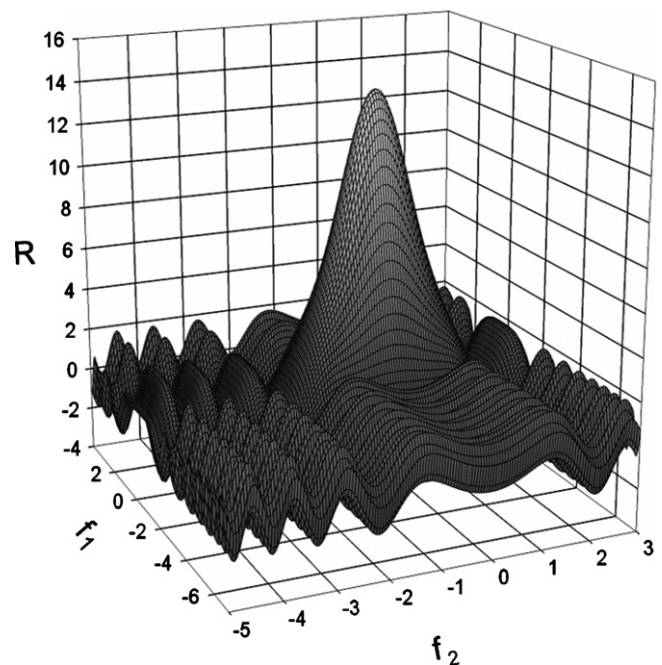

Fig. 3. Illustration of the paradigm behind the development of silicon-based composite electrodes. Development in this case goes through two distinctive steps: (i) determination of the important factors, defining the (*n*-dimensional) factor space $f_1, f_2, \ldots, f_n$, and (ii) finding the (possibly sharp) maximum of the cycle performance/reversibility in the factor space, which may be different for each particular active material–binder combination.

because the degree of lithiation is defined by the user. In the extreme case of a perfectly fabricated electrode there would be no need for any conditioning cycles and the electrode would be able to cycle without preconditioning at a higher capacity. Such an extreme condition is exemplified by a thin-silicon anode directly sputtered onto a roughened current collector [11,12]. In the latter case it is easy to understand that by simply maintaining mechanical contact between the silicon film and current collector as well as the mechanical integrity of the silicon film it is possible to ensure a long-lasting electrode. However, in the case of composite electrodes these important interactions are poorly understood. For example, it is widely believed that electrode materials that undergo large volumetric variations would exhibit better life cycle when bound on the current collector by means of elastomeric binders [13]. However, this suggestion is based on an intuitive perception and has not been evaluated numerically. Further, any evaluations that were performed were conducted by simply varying one factor at a time (i.e. the binder properties), while ignoring any interactions between possibly important parameters. Moreover, even similar silicon-based materials or lithium hosts that undergo large volumetric variations may actually exhibit different behaviors, and therefore, all hypotheses have to be checked thoroughly for each particular case (i.e. for each particular active material–binder combination).

The situation in the case of silicon-based composite electrodes is best summarized in Fig. 3, which does not represent any specific data, but rather is a conceptual model helping to describe the paradigm, required to develop this type of electrode. The response, R, is plotted as a function of two factors, f_1 and f_2. Although in general, there may be more than two of these factors, such a case cannot be geometrically represented. Therefore, Fig. 3 is just a necessary simplification giving a representative visual example. The first developmental step is to identify the important process factors ($f_1, f_2, \ldots, f_n$), defining n-dimensional space in which each dimension represents statistically significant factor f_i. The second step is to determine the possibly sharp maximum of the electrode cycle performance, as exemplified in Fig. 3. Note that whatever the factors $f_1, f_2, \ldots, f_n$, the best response is thought to be the coulomb efficiency when performing a constant capacity test with a fixed capacity from the first cycle. The paradigm schematically shown in Fig. 3 is completely different from that used in the case of intercalation hosts extensively studied in the past. In the case of intercalation hosts, research has focused on stabilizing the crystal lattice throughout the cycles or to modifying it in an appropriate way with respect to particular properties of interest, for example, current density or capacity. However, almost no attention has been paid to the electrode preparation since the crystal lattice itself determines the electrode properties. Electrode preparation
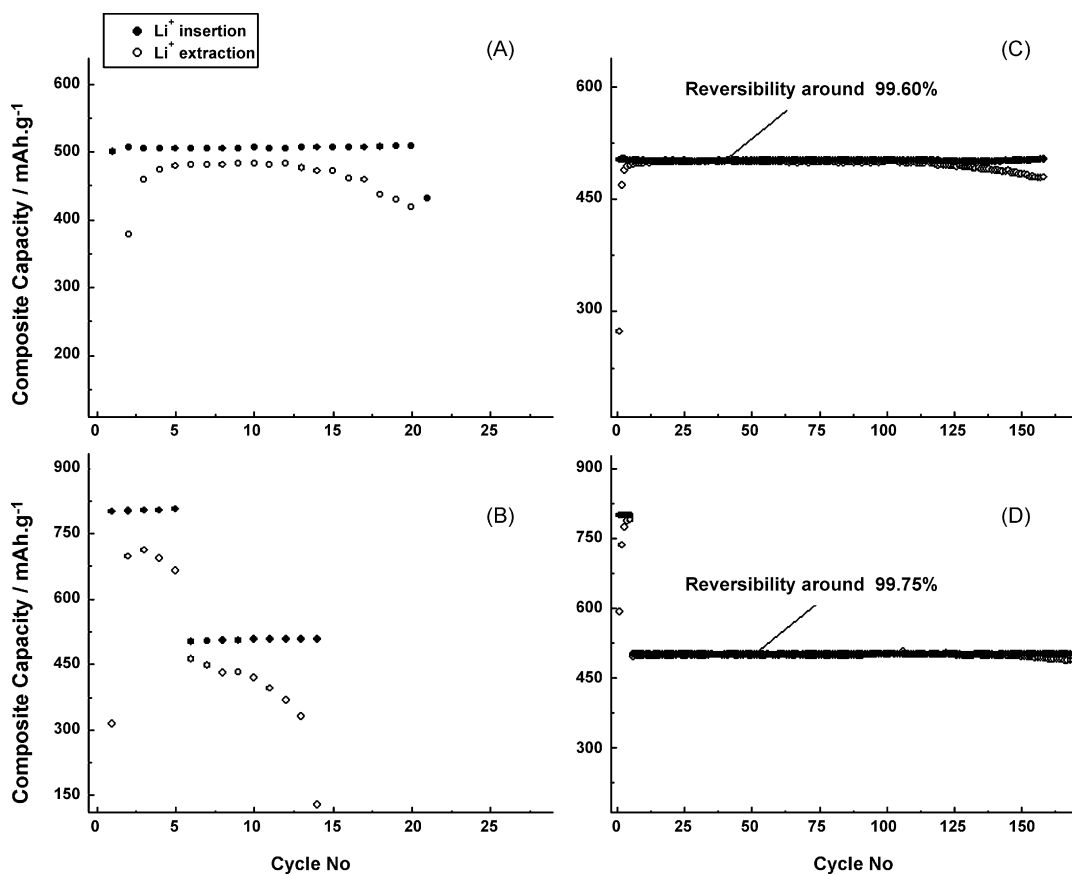

Fig. 4. Cycle performance of composite silicon-based electrodes. All electrodes contained the same active material (p-Si (1 μm): MCMB 6-28 1:1), had the same load density (around 2 mg cm^{-2}) and the same amount of binder (12.5 wt% of the weight of the dry electrode). The only difference was that A and B were prepared with standard PVdF binder, and C and D with CMC/SBR binder.

is therefore an easy step once we have tailored the properties of the intercalation host.

In the case of silicon-based composite anodes everything turned to be out completely opposite. For a sufficient life cycle the parent silicon crystal lattice must be converted into an amorphous state. In addition, it is important to keep the Li_xSi phase in its amorphous solid state. Since it is not a priori clear how to prepare and maintain a stable, reversible electrode structure, it is essential to take into account all the aforementioned details to obtain a long-lasting reversible electrode. Examples revealing the importance of both fundamental and technological features are given in the next section.

4. Results and discussion

Figs. 4 and 5 show the results of a cycle test of both types of composite silicon-based anode with and without preconditioning cycles. All electrodes were prepared with the same active material (see Section 2), and at approximately the same loading level ($2\,mg\,cm^{-2}$). The only difference is that electrodes A and B were prepared with standard PVdF binder (Kureha Co. Ltd.), while electrodes C and D with CMC/SBR binder (kindly provided by ZEON Co.). Striking difference between both cases suggests the crucial role of the binding system on the electrode performance. Since the role of the binding formulation cannot be predicted, constant capacity cycle test provides a convenient and reliable means of comparison between different binding formulations.

Figs. 4 and 5 suggest that simply performing conditioning cycles does not influence the life cycle of the poorly designed electrodes. On the contrary, the well-designed electrodes exhibit a moderate life cycle, despite a lack of conditioning cycles. Conditioning cycles in this case lead to a better coulomb efficiency: 99.75% in the presence versus 99.60% in the absence of conditioning cycles. Such a seemingly small difference might be important because to achieve a long lasting electrode, the corresponding electrochemical reaction should proceed with efficiency as close to 100% as possible. However, the effect of conditioning cycles is partly masked in half-cell configuration because as the cycling proceeds metallic lithium counter electrode turns into dendrite. It absorbs the electrolyte and in both cases the coin cells run almost in the absence of electrolyte in approximately the same cycle number. Therefore, half-cell configuration does not allow us to make a definitive conclusion regarding the importance of the initial conditioning cycles. However, it is notable that such a simple test protocols reveal directly the relative contribution of both the technological and the fundamental feature on each particular silicon-based composite electrode. We believe that these tests should be used in the following manner:

(1) Constant capacity cycle test with initial cycles performed at higher capacity (conditioning cycles), accounts for the relative contribution of the fundamental feature on the silicon composite electrodes. This means that it directly estimates the importance of an extra amor-
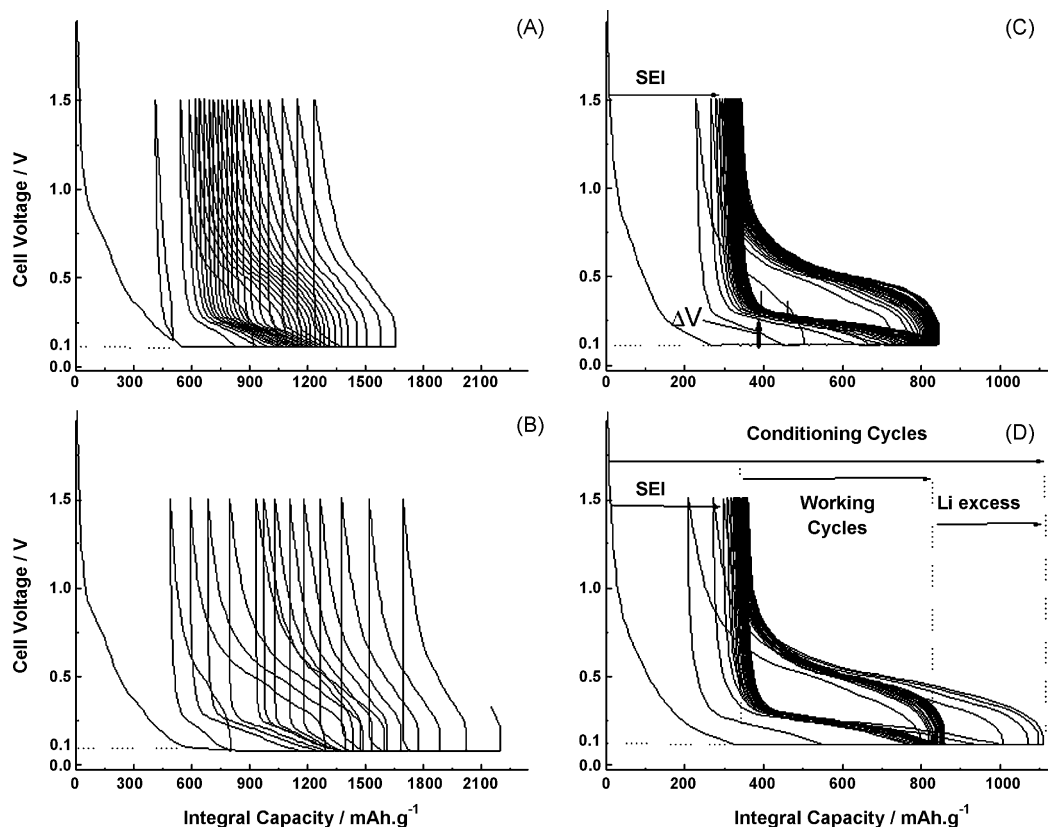

Fig. 5. Voltage profiles of the cells shows in Fig. 4. Lower voltage limit in all cases was set to 110 mV, well above the Li_xSi crystallization potential. Note the large polarization between the first and subsequent cycles, which occurred in all cases (A–D).

Table 1
Details of lithium-ion cells containing the composite electrode and various amounts of lithium to overcome the first irreversible capacity loss

Cell no.	Cathode weight (mg)	Anode weight (mg)	Li weight (mg)	Li-SEI equivalent (mAh g^{-1})	MBR
1	28.26	4.38	0.00	0.0	6.45
2	24.75	4.38	0.60	530	5.65
3	22.23	3.58	0.70	755	6.21
4	22.23	3.41	1.10	1250	6.52

The materials balance ratio (MBR) is defined as the cathode:anode weight. The Li-SEI equivalent was calculated according to Eq. (2). Charge/discharge current was set to 1 mA for all coin cells, which corresponds to 0.35–0.45 C-rate in a voltage window of 4.2–3.1 V.

phous silicon phase formed in situ during the initial cycles.

(2) Constant capacity cycle test performed at the same capacity from the first cycle, accounts only for the contribution of the fabrication technique or binding formulation.

In the case of perfect preparation technique or ideal binding formulation, the coulomb efficiency in both cases will coincide, i.e. there would be no difference between cases (1) and (2) when plotted in the same way as in Fig. 4. Data shown in Fig. 4 suggest that the technological feature plays a dominant role for improving this kind of electrodes.

It should be emphasized that a fixed capacity protocol can also be inaccurately used. That is, consider that only the first 20 or 50 cycles of the fixed capacity cycle protocol are plotted without the coulomb efficiency per cycle nor with mention of the cycle life; as well as being misleading, such data representation does not
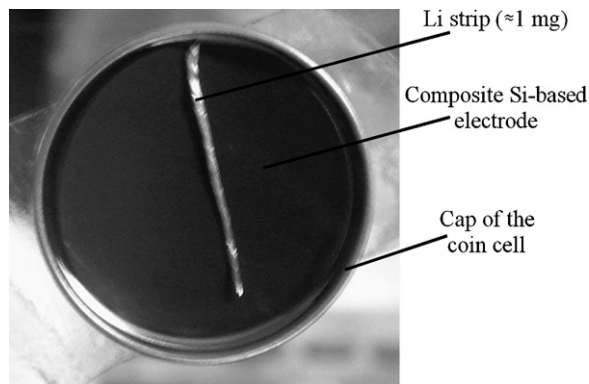

Fig. 6. Composite anode with a small amount of lithium placed on it to compensate for the SEI layer formation. Note that the lithium was cut in the form of a thin strip then simply placed on the composite anode.
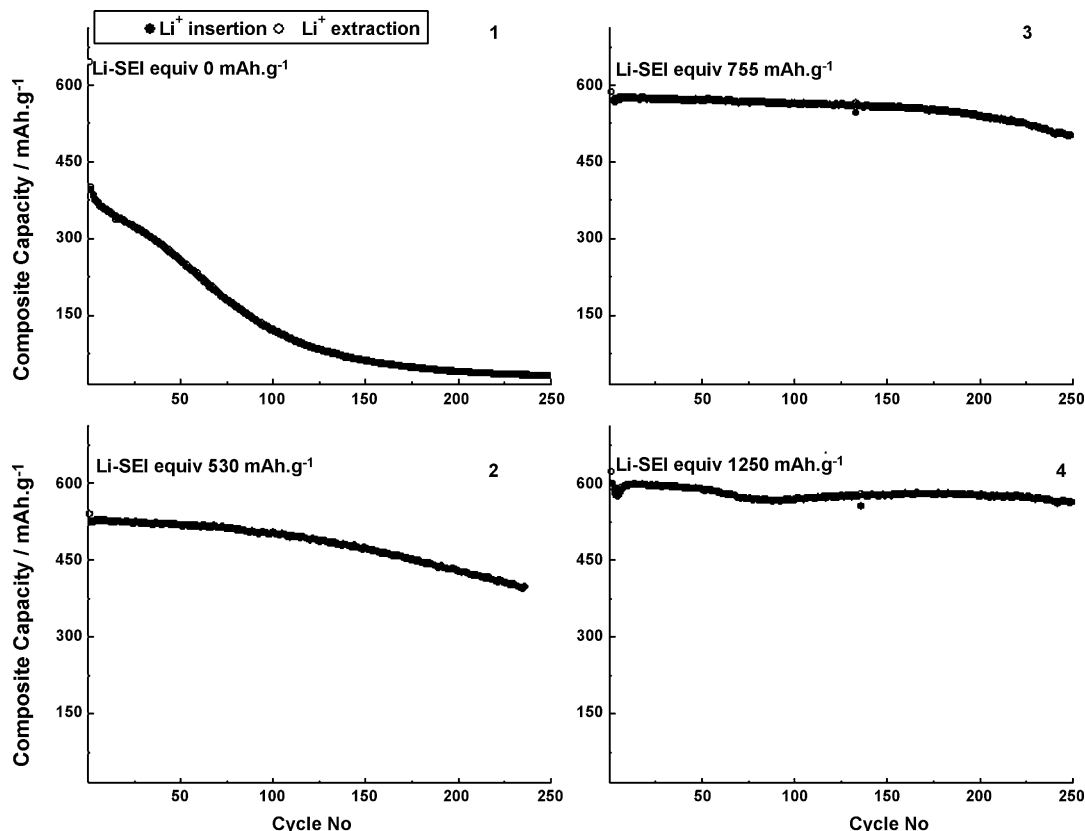

Fig. 7. Life cycle of lithium-ion batteries employing the new composite silicon-based anode. All cells contained the same anode and cathode with approximately the same material balance ratio. The only difference was in the amount of lithium added in order to compensate for the first cycle irreversible capacity loss.

suggest how reversible the electrode is. These examples clearly show that unique silicon electrochemistry requires rethinking of the method of data treatment and data interpretation.

The voltage profiles shown in Fig. 5 suggest that even electrodes with improved reversibility eventually need an extra lithium source in order to achieve a high-energy density and sufficient life cycle in a real lithium-ion battery. This situation is somewhat similar to that of transition tin oxides (TCO), which also need extra lithium source for the conversion reaction that takes place during the first cycle [14]. In this case, however, the extra lithium source may be needed in order to:

(i) saturate the SEI layer that forms during the initial cycles;
(ii) create a slight excess of lithium in the Li_xSi alloy, which is the equivalent of the conditioning cycles in the half-cell configuration.

It is convenient to define here the term lithium SEI equivalent. The term lithium SEI equivalent is used to represent a strictly defined (small) amount of lithium added to the negative electrode while assembling the cells. It is calculated by means of the following equation:

$$\text{SEI equivalent (mAh g}^{-1}) = \frac{3862 \times m_{Li}}{m_{Anode}} \quad (2)$$

where $3862\,\text{mAh g}^{-1}$ is the capacity of the metallic Li, m_{Li} the weight of the lithium added to the cell as an extra Li^+ source, and m_{Anode} is the weight of the active material (Si + MCMB in this case).

Obviously, the external Li source may overcome the initial capacity loss, and thus, may eventually allow cycling under the predefined conditions schematically shown in Fig. 5D. Such an electrode could therefore be regarded not only as composite and silicon-based, but also as a hybrid, a combination between metallic lithium and composite silicon electrodes. To some extent such an electrode should possess the high capacity of lithium and the safety of carbonaceous hosts, since the initially present small amount of lithium does not exist in its free form, but would be bound in both Li (SEI) and Li_xSi forms. Therefore, the silicon-based composite serves as a reservoir, accommodating the initially present free Li and the Li^+ from the cathode. A substantial advantage from an engineering viewpoint is that the properties of such electrodes can be tailored in order to exactly fit the need of a particular cathode material. It is well known that electrode properties depend strongly on their fabrication conditions, and therefore, one has to precisely balance both the cathode and anode materials connected to the poles.

Since composite silicon electrode properties are completely adjustable, they offer a wide range of possibilities. For example, it is possible to change the silicon content, the type and amount of conductive phase, and the degree of lithiation. From this viewpoint, our active material (p-Si: MCMB 6-28 1:1) is just one example of a reversible silicon-based electrode. Details of our lithium-ion batteries employing hybrid, composite silicon-based anodes are presented in Table 1.

Three important primary parameters are shown in the table: cathode weight, anode weight and Li weight. The logic when assembling this kind of cells is as follows. The cathode specific capacity (in our case $101\,\text{mAh g}^{-1}$) and cathode load level (mg cm^{-2}) define the required anode capacity. Since the capacity of the anode is adjustable (unlike intercalation hosts), changing the anode load level changes its working capacity. Bearing in mind the material balance ratio and required anode specific capacity we can then calculate the amount of lithium required to reach a predefined Li-SEI equivalent.

Fig. 6 shows an anode containing lithium proportional to a given SEI equivalent. Metallic lithium was cut in the form of a long narrow stripe and its weight was measured within an accuracy of approximately 0.1 mg. It was then placed on the composite electrode and the rest of the coin cell was assembled in a standard way. At present, it is not clear whether using a more homogeneously distributed, for example, stabilized Li powder lithium source would provide better results [15,16].

Fig. 7 shows the life cycle of various lithium-ion batteries, employing the same kind of anode and cathode (punched from the same electrode sheets) but containing various amounts of metallic Li (the various Li-SEI equivalents shown in Table 1). The data suggest there is strong synergy between the amount of the external lithium source and the cycle life of the LION
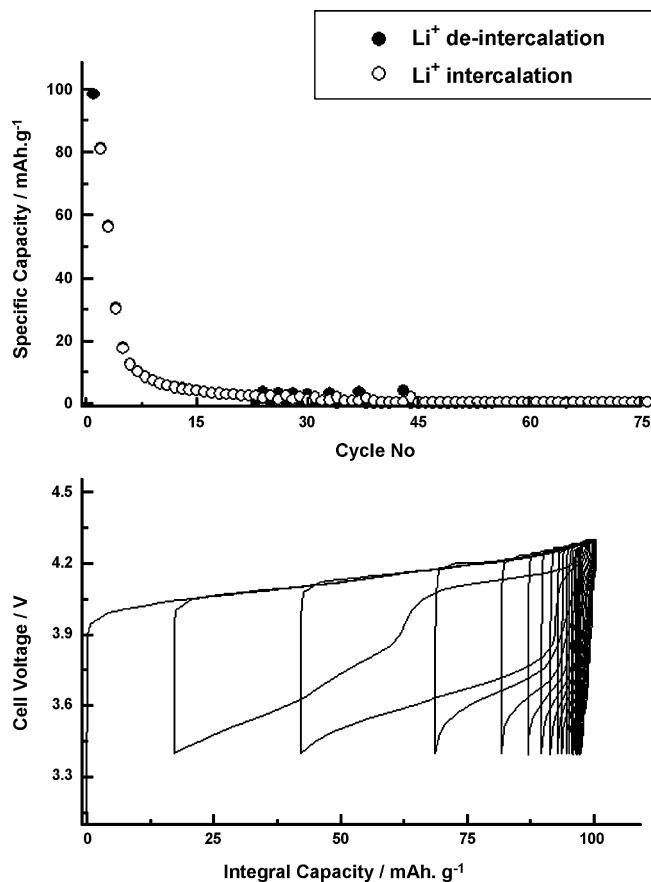

Fig. 8. Cycle life of a cathode punched from the same sheet as those used in Figs. 5–7 vs. a lithium strip ($\approx$1 mg) similar to the one seen in Fig. 4. The data clearly show that lithium in such a form and amount does not allow cycling of the cathode material.

cells. In general, larger amounts of initially added lithium led to a longer and more stable life cycle. The capacity with respect to the active negative material (i.e. Si + MCMB) lay within 500–600 mAh g^{-1}. It was notable that larger amounts of external lithium (larger Li-SEI equivalents) led to minima in the cycle number plots. Such behavior shows that there is evolution of the hybrid electrodes within the cycles; however, this needs to be clarified in more details in the future. Nevertheless, the data suggest that such electrodes may exhibit a satisfactory life cycle. The data and Table 1 also suggest that hybrid composite electrodes should be balanced, taking into account the total lithium content in the entire lithium-ion cell. Of coarse, ideally there would be no need for an extra lithium source, which would allow preparation of lithium-ion batteries using exactly the same facilities as when using graphite electrodes. We believe that even this goal may be possible at a higher degree of a composite electrode optimization. In addition Fig. 8 shows that the cycle life of these lithium-ion cells is not simply the result of the free Li present at the beginning of the test. The cycle life shown represents a cathode punched from the same sheet as those used in Figs. 5–7 versus a lithium strip ($\approx$1 mg) similar to the one shown in Fig. 4. The data clearly show that lithium in such a form and amount does not allow cycling of the cathode material, and therefore, Fig. 7 shows the life cycle of the hybrid electrode, not the initially present metallic Li versus the cathode material.

5. Conclusions

It has been long time intuitively recognized that silicon anodes for lithium-ion batteries should be considered in a specific manner, which takes into account their unique electrochemical properties. Rethinking of the research paradigm in this case is necessary because the electrochemical performance of these electrodes is completely dominated by the fabrication technology. Moreover, the usable capacity of the silicon anode is an adjustable parameter, meaning that the same electrode can be cycled at various capacities, resulting in various degrees of lithiation of the parent silicon phase. Thus, constant capacity cycling protocol of composite silicon anodes versus Li/Li$^+$ is an important test technique, which also serves as an appropriate analytical tool. It allows direct comparison of one electrode fabrication technique with another and one electrode composition with another. It also provides necessary normalization condi-

tions related to: (i) the degree of lithiation x in Li$_x$Si and (ii) the weight fraction of the parent Si alloyed with Li. Last but not in the least comparing constant capacity cycling tests including and excluding higher capacity initial cycles accounts for the relative contribution of both the fundamental and the technological feature responsible for the electrode performance.

Suggested cycle test when combined with appropriate experimental designs leads to a convergent procedure, which allows fast estimation of prospective binding formulations and/or fabrication techniques.

Acknowledgements

References

[1] M. Yoshio, T. Tsumura, N. Dimov, J. Power Sources 146 (2005) 10.
[2] N. Dimov, H. Noguchi, M. Yoshio, J. Power Sources 156 (2006) 567.
[3] H. Li, X. Huang, L. Chen, G. Zhou, Z. Zhang, D. Yu, Y.J. Moand, N. Pei, Solid State Ionics 135 (2000) 181.
[4] P. Limthongkul, Y.I. Jang, N.J. Dudney, Y.M. Chiang, J. Power Sources 119–121 (2003) 604.
[5] P. Limthongkul, Y.I. Jang, N.J. Dudney, Y.M. Chiang, Acta Mater. 51 (2003) 1103.
[6] M.N. Obrovac, L. Christensen, Electrochem. Solid State Lett. 7 (2004) A93.
[7] N. Dimov, K. Fukuda, T. Umeno, S. Kugino, M. Yoshio, J. Power Sources 114 (2003) 88.
[8] N. Dimov, S. Kugino, M. Yoshio, Electrochim. Acta 48 (2003) 1579.
[9] N. Dimov, S. Kugino, M. Yoshio, J. Power Sources 136 (2004) 108.
[10] M.N. Obrovac, L.J. Krause, International Meeting on Lithium Batteries, Biarritz France June 18–23, 2006 (Abs# 319).
[11] T. Yoshida, T. Fujihara, H. Fujimoto, R. Ohshita, M. Kamino, S. Fujitani, The 11th International Meeting on Lithium Batteries, Monterey CA June 23–28, 2002 (Abs# 48).
[12] S. Ohara, J. Suzuki, K. Sekine, T. Takamura, J. Power Sources 136 (2004) 303.
[13] Z. Chen, L. Christensen, J.R. Dahn, J. Electrochem. Soc. 150 (2003) A1073.
[14] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, Science 276 (1997) 1395.
[15] C.R. Javris, M.J. Lain, Y. Gao, M. Yakovleva, J. Power Sources 146 (2005) 331.
[16] C.R. Javris, M.J. Lain, M.V. Yakovleva, Y. Gao, J. Power Sources 162 (2006) 800.