

Short communication

## Towards creating reversible silicon-based composite anodes for lithium ion batteries

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### Abstract

A new inexpensive method aimed at distinguishing the forms in which  $\text{Li}^+$  remains irreversibly trapped within composite silicon-based anodes was suggested and tested. It includes a life-cycle test at a fixed degree of lithiation during the initial cycles. The integral capacity values obtained from the test were then correlated with the various chemical species of  $\text{Li}^+$  present in the electrodes after various cycle numbers in both charged and discharged states. Such a technique may provide a quantitative analytical tool for developing this type of electrode.

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### 1. Introduction

Recently, anode materials for lithium ion batteries (LION), based on the alloying type of the electrochemical reaction have attracted attention worldwide [1–3]. Among these, silicon is regarded the most attractive candidate due to its low-atomic weight and the possibility of achieving a high Li mole fraction in Li–Si alloys. However, despite these favorable properties, silicon-based composite anodes are yet to be commercialized due to the large volumetric variation in the pristine silicon phase during the initial cycle, which makes such electrodes unstable. Another feature of these electrodes is the potential gap between the first and the subsequent cycles. The situation is further complicated by the texture of the electrode, which influences the voltage profile. Therefore, more reliable and reproducible results are obtained when limiting the capacity (and thus  $x$  in  $\text{Li}_x\text{Si}$ ), instead of only the voltage window or current density, as is the case for all intercalation hosts. This approach which was used by us previously [4], serves as a normalizing condition; however, although necessary, such normalization is not sufficient for drawing quantitative conclusions. An important additional indication of the quality of the electrode is the integral capacity loss (ICL) value and its cycle-to-cycle variation. However, most researchers [1–17] do not perform such an analysis mainly because ICL occurs as a result of two concurrent processes:

- (i) solid electrolyte inter-phase (SEI) formation;
- (ii) accumulation of  $\text{Li}^+$  in the bulk of the material in the form of  $\text{Li}_x\text{Si}$  and  $\text{Li}_x\text{C}_6$  in the case of mixed Si/C composites.

Thus, it is essential to distinguish the chemical species responsible for trapping  $\text{Li}^+$  within the active material. To the best of our knowledge such analysis has not been performed to date. The problem is that most instrumental methods, such as XRD, are designed to provide information specific to solid phases with well-defined crystal lattices, i.e. intercalation hosts. Since the reaction here is electrochemical alloying, not intercalation, the standard methods of studying intercalation hosts are not particularly helpful. It is therefore surprising that virtually all studies regarding composite silicon-based anodes follow the same paradigm: observation of crystal lattice destruction (amorphous phase formation) and morphological changes observed in SEM or TEM images. Such an approach does not allow quantitative conclusions and does not suggest how lithium remains trapped within the active material. Nevertheless, such information may be very helpful for choosing a research strategy. For example, if lithium remains trapped within the SEI layer, electrolyte improvement may be needed. On the contrary, if  $\text{Li}^+$  is rapidly accumulated within the bulk of the material in the form  $\text{Li}_x\text{Si}$ , changes to the electrode itself and/or the binder may be necessary.

In the present study, a simple method for distinguishing between the chemical species responsible for  $\text{Li}^+$  irreversible loss is proposed and tested. It is based on the assumption that the SEI layer consist of inorganic and organic salts such as  $\text{Li}_2\text{CO}_3$ ,  $\text{LiF}$ , and  $\text{LiOCOOR}$ , which do not release gases upon contact

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with water. On the contrary,  $\text{Li}^+$  trapped within the bulk of the silicon is accumulated in the form  $\text{Li}_x\text{Si}$ , and moreover, reacts with water releasing gases the volume of which can be precisely measured. Such a method would enable the chemical forms of irreversibly bound  $\text{Li}^+$  to be determined, and therefore, may be regarded as a method of chemical speciation.

## 2. Experimental part

Two kinds of mixed Si/C composites were prepared containing 50 wt% p-Si (average particle grain size  $1\ \mu\text{m}$ ) and 50 wt% MCMB 6-28 (Osaka Gas Chemical, Japan) or acetylene black (AB), respectively. In both cases, the composite was premixed for 1 h in a planetary ball mill (Fritsch, Germany) at 250 rpm. Balls:active material weight ratio was set at approximately 10:1. The active material was bound onto a copper foil current collector by means of an aqueous styrene-butadiene copolymer binder (SBR, commercial designation BM-400B, ZEON Co., Japan). Sodium carboxy methyl cellulose (CMC, commercial designation HB-45, ZEON Co., Japan) was used as a thickening/setting agent. Dry electrode contained 84 wt% active material and 16 wt% binder (SBR + CMC). From the copper foil, circular electrodes with a diameter of 1.8 cm were punched. Their mass and thickness were then measured and coin cells were assembled. Cycling was performed in 1 M  $\text{LiPF}_6$  dissolved in EC:MEC 3:7 (UBE Chemicals, Japan). After a given cycle number, the coin cells were stopped in either a charged ( $\text{Li}^+$  insertion) or discharged ( $\text{Li}^+$  extraction) state. They were then disassembled and excess electrolyte absorbed by a dry tissue. Electrodes were sealed in small polypropylene envelopes and taken out of the glove box. Built-in-house equipment was used to measure the amount of released gases, as shown in Fig. 1.

The apparatus shown in Fig. 1 consists of a plastic container filled with water, a funnel attached to a burette connected to a thin glass tube (inner diameter 2.4 mm) for collecting and measuring the volume of gases released upon reaction of the cycled electrode with water. The upper end of the thin glass tube was connected to a peristaltic pump. Before measurement, the entire system was filled with water; after that the peristaltic pump was stopped and valve 7 closed. The polypropylene envelope containing the cycled electrode was then immersed in the vessel beneath the funnel and cut. After completion of the reaction, valve 7 was opened and the peristaltic pump turned on until the gas moved into the thin glass tube (#8 in Fig. 1). The length of the gas layer was then measured, and the procedure was repeated with the next electrode. Internal cell resistance was also measured by means of a Solartron SI 1250 frequency response analyzer (USA) at 60 kHz with a superimposed signal with an amplitude of 5 mV.

### 2.1. Verification of the method

To the best of our knowledge, the above method has not been used until now. It should also be noted that the built-in-house equipment should be checked and calibrated prior to use. To confirm the accuracy of this procedure, a number of preliminary experiments were performed. First, it was important to

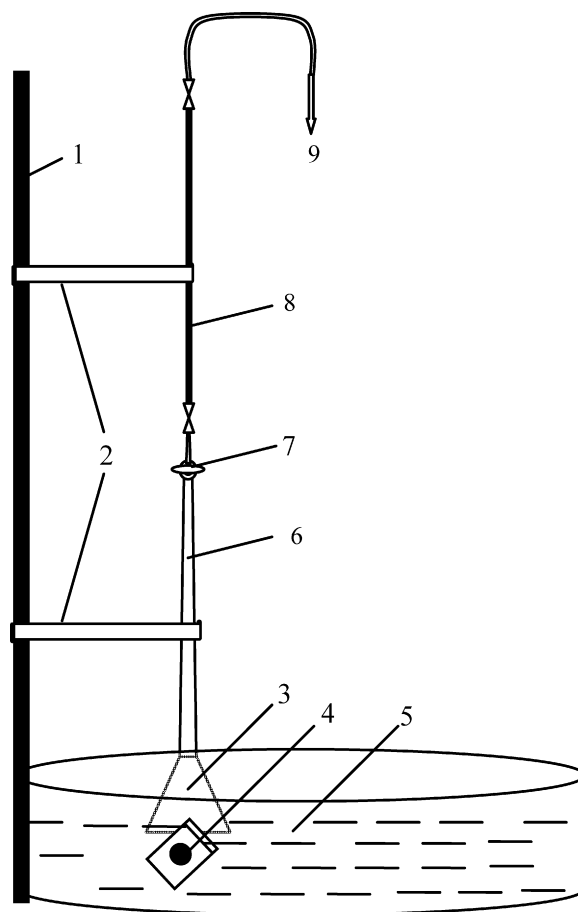
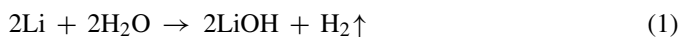


Fig. 1. Sketch of the built-in-house equipment used to measure the amount of gases released from the silicon composite electrode upon reaction with water: (1) stand, (2) holders, (3) funnel, (4) electrode sealed in a polypropylene envelope, (5) vessel filled with water, (6) burette, (7) valve, (8) capillary (inner diameter 2.4 mm) and (9) tube to the peristaltic pump.

confirm that the released hydrogen is not dissolved in the water considerably. To check this, small pieces of lithium with a precisely measured mass were sealed in polypropylene envelopes. The envelopes were then immersed beneath the funnel (#3 in Fig. 1) and cut. The volume of released hydrogen was subsequently measured and the amount of gas released per unit mass of lithium ( $\text{ml mg}^{-1}$ ) was calculated. For convenience this value was defined as a gas equivalent (GE) ( $\text{ml mg}^{-1}$ ) and is used accordingly throughout. Six consecutive measurements gave an average value of  $1.69 \pm 0.1\ \text{ml mg}^{-1}$ . Taking into account that in this case hydrogen evolves according to the following reaction:

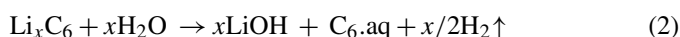


it follows that the theoretical Li gas (hydrogen) equivalent is  $1.614\ \text{ml mg}^{-1}$  under normal conditions (101325 Pa and  $25\ ^\circ\text{C}$ ). Therefore, the measured lithium GE was somewhat higher than predicted. This can be explained by the slightly smaller atmospheric pressure than defined as normal (101325 Pa at  $25\ ^\circ\text{C}$ ). There are also small variations in the atmospheric pressure; however, since these do not usually vary by more than 5%, such accuracy is acceptable in further clarifying the validity of our technique. Thus, no correction for this atmospheric pressure

variation was performed and the system was held open to the atmosphere. The most important conclusion from this preliminary test was that the volume of the released hydrogen can be reliably measured with the proposed procedure.

The second step of the verification procedure was to measure the volume of gas released from both phases,  $\text{Li}_x\text{C}_6$  and  $\text{Li}_x\text{Si}$ , at various degrees of lithiation. Both  $\text{Li}_x\text{C}_6$  and  $\text{Li}_x\text{Si}$  were separately prepared using pure MCMC 6-28 and Si electrodes assembled in coin cells. Both types of electrode were lithiated to strictly defined Li mole fractions and the amount of released gas upon reaction with water was measured.

Reaction of  $\text{Li}_x\text{C}_6$  with water is expected to proceed according to the following equation:



From Eq. (2) it follows that the gas equivalent of  $\text{Li}_x\text{C}_6$  with respect to the pristine MCMC is given by

$$\text{GE}_{\text{Li}_x\text{C}_6} = \left( \frac{(x/2) \times 22400}{72 \times 1000} \right) = 0.1556x \quad (3)$$

where  $x$  is the mole fraction of Li in  $\text{Li}_x\text{C}_6$ , 22,400 ml is the volume of one mole of ideal gas at 101,325 Pa and 25 °C, 72 is the molecular weight of the unit  $\text{C}_6$ , and 1000 was employed to convert grams into milligrams.

The data, its linear fit and a comparison of the theoretical and experimental results are given in Fig. 2. The calculated and measured values coincided quite well, suggesting that this method can be used with respect to the pure lithiated carbonaceous phase. In theory, the slope in Eq. (3) should be equal to 0.1556; however, fitting the data in Fig. 2 gives:

$$\text{GE}_{\text{Li}_x\text{C}_6} = 0.0045 + 0.1436x \quad (4)$$

This deviation implies that there might be extra gas release (for example  $\text{C}_2\text{H}_4$ ) at smaller degrees of lithiation, thus decreasing

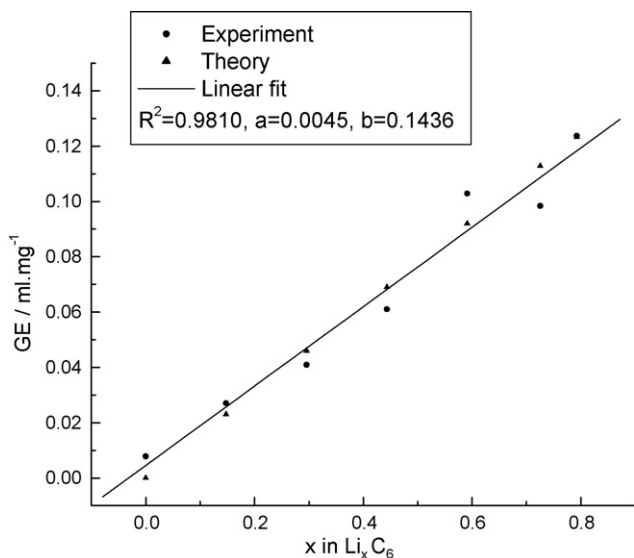
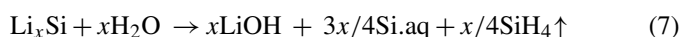
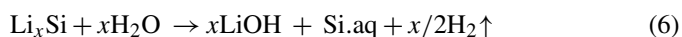
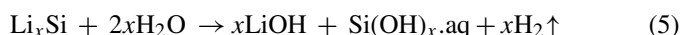


Fig. 2. Amount of the gas evolving from the MCMC 6-28 electrode upon reaction with water as a function of the lithium mole fraction. The measured data coincided well with the values calculated according to reaction (2).

the slope obtained by fitting the experimental data. This effect has yet to be studied in detail, because the error induced by such variation is thought to be within several percent and is therefore acceptable in this preliminary investigation.

In the case of  $\text{Li}_x\text{Si}$  the situation is somewhat more complicated because there are at least three possible reaction schemes. Moreover, reaction products and therefore the released gas volume may depend on the degree of silicon lithiation. The corresponding reactions can be represented as follows:



In case (6), only Li present in the alloy releases hydrogen, whereas in case (5) silicon equivalent to the amount of Li present in the alloy also reacts with water and therefore the amount of hydrogen doubles compared to case (6). In case (7), the amount of released gas is only a quarter of that in case (5). The corresponding quantitative expression of the gas equivalent with respect to the pristine Si in this case is:

$$\text{GE}_{\text{Li}_x\text{Si}} = \left( \frac{a \times 22400}{28.08 \times 1000} \right) = a \times 0.7977 \quad (7)$$

where 22,400 ml is the volume of one mole of ideal gas at 101,325 Pa and 25 °C, 28.08 is the atomic weight of Si, 1000 was employed to convert grams into milligrams,  $a=x$  in case (5),  $a=x/2$  in case (6), and  $a=x/4$  in case (7), and  $x$  is the mole fraction of Li in the Li/Si alloy.

The data, its linear fit and a comparison of the theory (cases (5), (6) and (7)) and experimental results is given in Fig. 3.

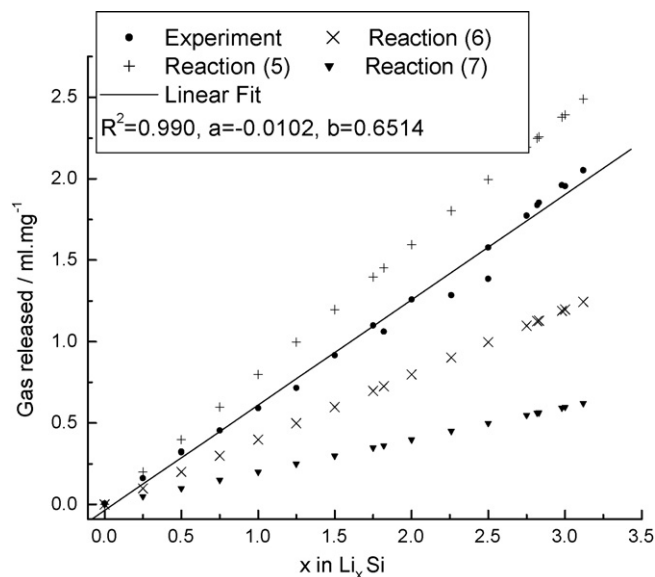


Fig. 3. Amount of the gas evolving from the pure Li/Si electrode upon reaction with water as a function of the lithium mole fraction. Theoretical predictions according to the various reaction schemes discussed throughout the text are compared with the experimental data; the straight line represents the linear fit of the experimental data.

Fig. 3 suggests that neither scheme (5) nor scheme (6) can completely explain the data. Although this reaction seems to proceed in an intermediate regime (i.e. a combination of (5) and (6)), the amount of released gases remains linear as a function of the degree of silicon phase lithiation, at least within  $0 \leq x \leq 3.1$ . Therefore, it can be adopted as an analytical tool in the same way as in the case of  $\text{Li}_x\text{C}_6$ . From the data presented in Fig. 3 it follows that:

$$G_{\text{E}_{\text{Li}_x\text{Si}}} = -0.011 + 0.6514x \quad (8)$$

Since alloys with a higher degree of lithiation (at approximately  $x > 1.5$ ) were obtained at a constant potential of 5 mV versus Li, one might suspect lithium deposition rather than  $\text{Li}_x\text{Si}$  formation only. However, lithium deposited in a detectable excess is unlikely because after resting the cells their open circuit voltages were well above 5 mV, in a range of 30–150 mV, suggesting that the large polarization was caused by kinetic reasons and the final equilibrium Li–Si alloy versus metallic lithium did not contain free metal.

The data in Fig. 3 also suggest that electrochemically formed  $\text{Li}_x\text{Si}$  in its pure form does not produce, or produces only a small fraction, of  $\text{SiH}_4$  or higher silanes; otherwise there would be negative deviation in Fig. 3 (i.e. below the line accounting for case (6)), but this was not observed experimentally. One possible explanation for this may be that the reaction between the electrochemically formed Li–Si alloy and water proceeds vigorously and, at higher degrees of lithiation, almost explosively and therefore, any silanes will decompose instantly. MAS-spectra of the gaseous phase did not indicate the presence of any compounds with a molecular weight higher than 32, i.e. corresponding to  $\text{SiH}_4$ . Therefore, under these conditions the only possible by-product seems to be  $\text{SiH}_4$  in sufficiently small amounts unable to significantly influence the volume of evolving gases.

### 3. Results and discussion

Cycle test results for both types of electrode (containing AB and MCMB 6-28 as conducting phases, respectively) are shown in Fig. 4. Both electrodes had the same elemental composition (i.e. Si and C 1:1 by weight as an active material) and the same amount and type of binder.

Nonetheless, their life cycles differed considerably. Electrodes containing 50 wt% of the active mass of AB deteriorated very quickly and could not be cycled for more than 40–50 cycles at  $500 \text{ mAh g}^{-1}$ , whereas those employing MCMB 6-28 as a conductor could be cycled for approximately 200 cycles at  $500 \text{ mAh g}^{-1}$ . The latter electrodes are therefore a convenient model for checking the validity of the proposed method. The best way to apply this method would be to compare either the integral capacity (IC) or integral capacity loss (ICL) for charged and discharged states, respectively, with the amount of released gases as cycling proceeds. Both IC and ICL are defined in Fig. 5. Actually, the integral values (IC and ICL) are exactly equivalent to the corresponding amount of  $\text{Li}^+$  remaining trapped within the electrode in one out of the three forms: Li(SEI),  $\text{Li}_x\text{C}_6$  and

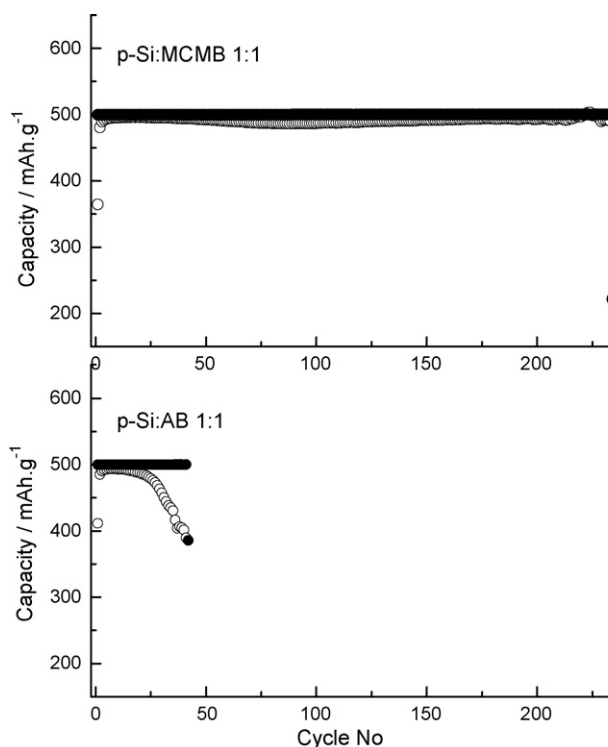


Fig. 4. Life cycles of the two types of composite electrode. Different life cycles were observed despite the fact that the electrodes contained active material with the same elemental composition and the same amount and type of binder. The data were directly comparable due to the normalized conditions of the test.

$\text{Li}_x\text{Si}$ , and can therefore be used for precise characterization of composite silicon-based electrodes.

One more favorable feature of the proposed method is also suggested; that is, the different gas equivalents for both phases,  $\text{Li}_x\text{C}_6$  and  $\text{Li}_x\text{Si}$  (i.e. slopes 0.1436 and 0.6514 in Eqs. (4) and

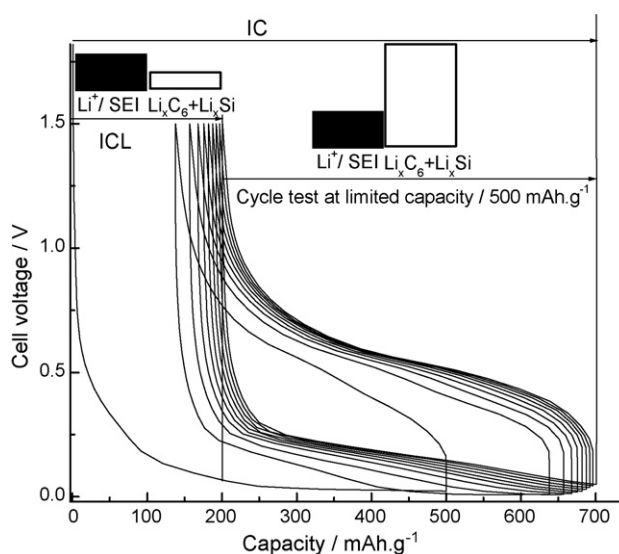


Fig. 5. Definition of the integral capacity (IC) and integral capacity loss (ICL) values used to study the composite silicon anodes. The difference between the IC and ICL for any fixed cycle number was used as a direct estimate of the lithium irreversibly accumulated in one out of the three forms: Li(SEI),  $\text{Li}_x\text{C}_6$  and  $\text{Li}_x\text{Si}$ .



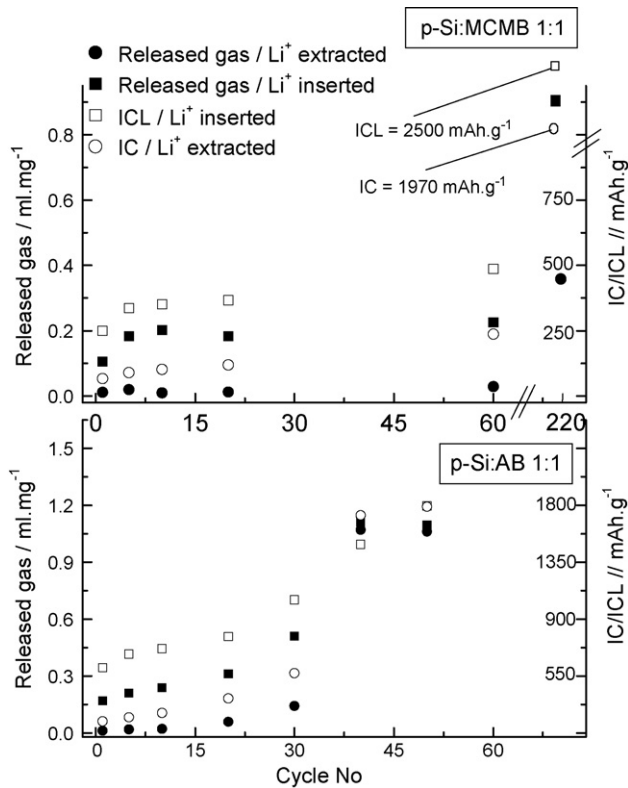


Fig. 6. Amount of gas released at various cycle numbers and charging states. Note that the electrode with a short life cycle quickly accumulated Li in the form of  $\text{Li}_x\text{C}_6/\text{Li}_x\text{Si}$ , proportional to the amount of released gases. On the other hand the electrode with a better life cycle accumulated these forms of  $\text{Li}^+$  much slower and increased ICL values were caused mostly by SEI formation.

(8), respectively), enable further data fitting and clarification of the form in which Li remains in the bulk of the material (i.e.  $\text{Li}_x\text{C}_6$  or  $\text{Li}_x\text{Si}$ ). Ideally, not only lithium accumulated in the bulk ( $\text{Li}_x\text{C}_6 + \text{Li}_x\text{Si}$ ) and Li(SEI) may be distinguished, but also the amount of lithium trapped by either  $\text{Li}_x\text{C}_6$  or  $\text{Li}_x\text{Si}$  may be detectable.

Fig. 6 shows the amount of released gases as a function of the cycle number for both types of electrode in both a charged ( $\text{Li}^+$  extracted) and discharged ( $\text{Li}^+$  inserted) state. Unfortunately, these data did not fit with the slopes obtained from Figs. 2 and 3 (Eqs. (4) and (8)). The only way to roughly adjust the data was to suppose that the gas equivalent of  $\text{Li}_x\text{Si}$  was not 0.6514, but rather around 0.2 which corresponds to reaction (7), i.e.  $\text{SiH}_4$  formation. The most likely explanation is that  $\text{Li}_x\text{Si}$  in the presence of  $\text{Li}_x\text{C}_6$  reacts with water giving different final products. Reaction of the mixture  $\text{Li}_x\text{Si} + \text{Li}_x\text{C}_6$  with water proceeds in a very moderate fashion compared with the case of pure  $\text{Li}_x\text{Si}$ . Under such conditions, the formation of  $\text{SiH}_4$  probably becomes kinetically favorable. A possible way to overcome this obstacle and exploit the full capability of the method would be to use the slope in Eq. (8) as an adjustable parameter and at the same time perform quantitative analysis of the released gases, assuring consistency between the adjusted values and reaction products. However, quantitative analysis of such a gaseous phase was not possible at the time of the experiment, and therefore, the data could only be used semi-quantitatively.

Fig. 6 implies that even semi-quantitative (without distinguishing the contributions of  $\text{Li}_x\text{Si}$  and  $\text{Li}_x\text{C}_6$ ) data provide very useful information. It can clearly be seen that the amount of released gas increased sharply just before the end of the cycle test, when the electrode deteriorates irreversibly. This amount is proportional to  $\text{Li}^+$  trapped in the state ( $\text{Li}_x\text{Si} + \text{Li}_x\text{C}_6$ ), and therefore, accumulation of  $\text{Li}^+$  can be directly associated with electrode deterioration. Moreover, at 40th and 45th cycles the electrodes released almost the same amount of gas in a charged and discharged state. This clearly indicates that there is a critical point of lithium supersaturation, beyond which the electrodes irreversibly break down and lithium cannot be extracted. On the contrary, the electrode with a longer cycle life showed a very small increase in the amount of released gases up until cycle number 60. The ICL values shown in Fig. 6 therefore seem mainly due to SEI accumulation.

Further insight into the processes taking place during cycling is given in Fig. 7. This figure again represents only measurable numerical values; namely changes in internal cell resistance as the cycling proceeds.

Cell internal resistance was measured in order to monitor the condition of the entire cell, not only the electrode. Since the silicon-based composites have a large capacity, a large amount of lithium is necessary in order to assure sufficient Li excess. However, it turns into dendrite which then absorbs the electrolyte, giving rise to increased cell resistance. As seen in Fig. 7, at least for cycle numbers up to 60, this is not a problem and as expected,

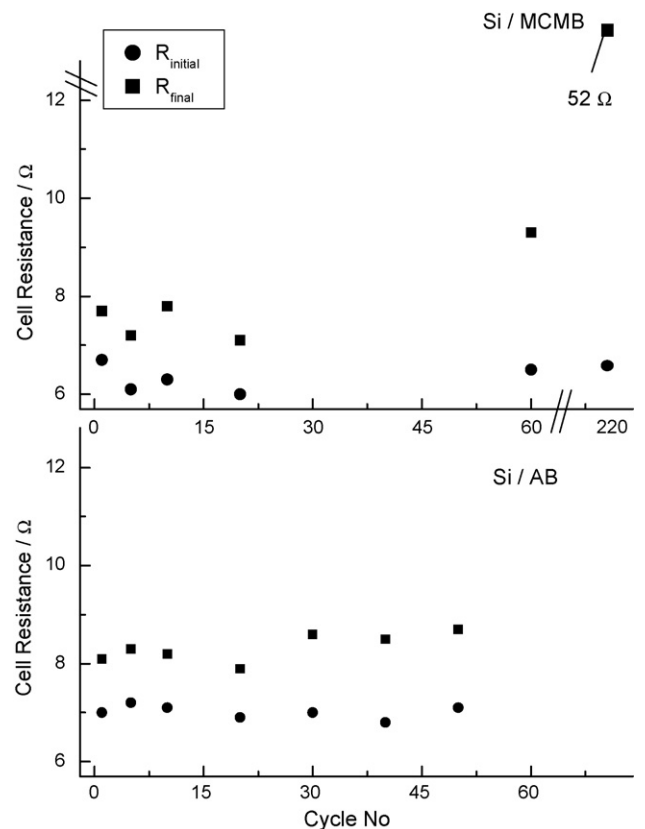


Fig. 7. Variation in cell internal resistance for cells containing both types of composite electrode.

after 200 cycles most of the lithium turned into dendrite and the interior of the cell became almost dry. Therefore, in this case, the effects of the ageing of the composite itself and changes in the cell's internal conditions are superimposed. A possible way to overcome this well-known limitation of coin cells, containing metallic Li might be to decrease the amount of active material. However, such electrodes are, in most cases, sensitive to the active material loading density ( $\text{mg cm}^{-2}$ ), and therefore, such results are not directly comparable. Moreover, from an engineering viewpoint there is almost no meaning to working with electrodes delivering less than 1 or 2 mAh  $\text{cm}^{-2}$ . Therefore, a different kind of cell, one containing more electrolyte should be used. Unfortunately, changing cell configuration is not a trivial task for this kind of electrodes and thus for the moment it is not clear whether the electrodes would provide better results if different test cells were employed.

#### 4. Conclusions

A new inexpensive method aimed at distinguishing the forms in which  $\text{Li}^+$  remain irreversibly trapped within composite silicon-based anodes was suggested and tested. Despite its simplicity and the fact that it is unlike most instrumental methods presently employed, this technique provided only measurable values. Thus, cycling Si-based anodes under normalized conditions (i.e. a predefined value of  $x$  in  $\text{Li}_x\text{Si}$  during the initial cycles) and comparing the integral values of IC/ICL with the amount of released gases upon reaction with water provides quantitative chemical evidence of the processes responsible for their failure. We believe that such a method, or a similar kind of Li chemical speciation, may play an important role in improving and optimizing these electrodes. Moreover, this method partly fills the need for a chemical analytical tool in this field of study.

#### Acknowledgment

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