Study and modeling of the Solid Electrolyte Interphase behavior on nano-silicon anodes by Electrochemical Impedance Spectroscopy

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ABSTRACT

The instability of the Solid Electrolyte Interphase (SEI) at the surface of nano-silicon electrodes has been recognized as one of the key issues to explain the rapid capacity fading of these electrodes. In this paper, two distinct Si-based systems are studied by using Electrochemical Impedance Spectroscopy (EIS). First, several EIS spectra are recorded along the second electrochemical cycle. Although the active material, the electrode formulation, and the experimental conditions are different for the two systems, the same phenomena are observed in both cases: (i) the SEI deposit around 50 kH, (ii) the charge transfer (CT) with a characteristic frequency varying from 300 to 10 000 Hz, and (iii) an inductive loop at ~1 Hz which appears only when the potential of the electrode is below 0.35 V vs Li. As the latter has never been reported for Si-based electrodes, the second step of the work consists in understanding this phenomenon. Thanks to the results obtained in a set of several complementary experiments, we finally attribute the inductive loop to the constant formation/deposition of SEI products, in competition with the CT process. In addition, we propose a mechanism for this specific phenomenon and the equivalent circuit to fit the recorded EIS spectra.

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1. Introduction

In the past two decades, the demand for high-capacity Lithium-ion Batteries (LIBs) for portable electronics, hybrid electric vehicles, and large scale energy storage has stimulated the research for new electrode materials [1–3]. Concerning negative electrodes: metals and semi-metals that can electrochemically form alloys with lithium represent a relevant alternative to carbon-based anodes [4,5]. Silicon is considered as one of the leading candidates: the fully lithiated state of silicon at room temperature is Li15Si4 which corresponds to a capacity of 3 580 mAh g−1, ten times larger than that of graphite [6]. Nevertheless, silicon undergoes huge volume changes upon alloying and de-alloying with lithium: up to +300% compared to the initial volume for a full lithiation [7]. These volume changes are responsible for strong mechanical strains inside both the silicon particles and the bulk composite electrode and subsequent loss of electrical contacts between the active material, the conductive matrix and the current collector resulting in poor cyclability for Si-based electrodes [4,5]. To improve these electrochemical performances, many studies concerning the silicon material itself [8], the binder [9,10], and/or the formulation [11,12] have been carried out and the performances have been very much improved in recent years. As an example, thanks to the use of nanoparticles, Si particles integrity can be maintained even when they are cycled at high capacities [8,13]. However, despite these promising results, cycling performances of Si electrodes, particularly in terms of coulombic efficiency, remain so unsatisfactory for a use in practical LIBs.

Indeed, one of the strong limitations has been recognized to be directly linked to electrode/electrolyte interfaces [14–16]. Upon cycling, the electrolyte standardly made of LiPF6 dissolved in organic carbonates is reduced and the resulting reduction products constitute a Solid Electrolyte Interphase (SEI) at the Si electrode surface. By using X-ray Photoelectron Spectroscopy (XPS), SEI composition which forms on Si electrodes has been found to be similar.
to that observed on graphite: it is mainly made of lithium alkyl carbonates, lithium carbonate, and other lithium inorganic salts [14–16]. Nevertheless, volume changes of Si particles can cause an important instability of this SEI. At each cycle, SEI reconstruction may consume lithium, electrolyte components, and electrons, consequently contributing to the aforementioned irreversible capacity and low coulombic efficiency. The behavior of this SEI upon cycling appears then as one of the key parameters governing the practical electrochemical performances of Si electrodes.

Electrochemical impedance spectroscopy (EIS) has proven to be a powerful technique to study the different aspects of electrode kinetics, interfacial changes and especially the SEI formation [17–25]. However, only few studies with detailed EIS characterizations on silicon anodes are available in literature.

As EIS measurements can be very specific to active materials (morphology, surface treatment, etc.) and also depend on experimental conditions (electrochemical cell, reference electrode, electrodes alignment, etc.), we chose in this paper to carry out EIS analyses on two different systems. For both cases, the active material, the formulation and the experimental conditions to acquire the spectra are different.

2. Experimental

2.1. Materials

Two different silicon nanopowders, called here Si1 and Si2, were used. Si1 is a commercial nano-Si from Umicore, with an average diameter of 50 nm, a specific surface area of 23 m².g⁻¹ and an oxide layer thickness of ~3 nm. Si2 is made of 150 nm diameter particles; its specific surface area is close to 13 m².g⁻¹ and the oxide layer is very thin (<1 nm). SEM and TEM characterizations of both materials are available in ESI.

2.2. Electrode fabrication and electrochemical testing

Si1 and Si2 based slurries were used to realize the electrodes. Si1-slurry was an aqueous mixture of Si1 silicon (80 wt %), super P (12 wt %), and CMC (8 wt %), whereas Si2-slurry was made of Si2 silicon (65 wt %), carbon fibers (25 wt %) and CMC (10 wt %). By using a doctor blade, both slurries were coated at a thickness of 100 μm on a copper foil current collector and dried 24 h at 80 °C. For both electrodes, the final loading was ~2 mg of Si per cm², suggesting a porous nature of these as-prepared anodes. For Si1, electrodes were cut into 11 mm diameter disk shape, dried 3 h at 150 °C and transferred into an argon-filled glove box. 3-electrodes Swagelok®-type cells were then assembled. For Si2, 17 × 35 mm² rectangular electrodes were cut, dried 48 h and assembled in 3-electrodes pouch-cells in an anhydrous room. For both types of cells, the counter and the reference electrodes are made of metallic lithium. The electrodes are separated by glass fiber separators soaked with a liquid electrolyte (1 M LiPF6 in ethylene carbonate (EC): diethyl carbonate (DEC) wt % of 1:1). In specific cases, 10 wt % of FEC was also added.

Galvanostatic charges and discharges were carried out with a Maccor® battery tester for the Swagelok® cells (Si1) and a VMP3 Biologic® system for the pouch cells (Si2).

2.3. EIS measurements

All the EIS measurements were performed after relaxing the cell until the deviation of the potential was inferior to 1 mV.h⁻¹. For Si1, the perturbation amplitude was 5 mV and the frequency range was scanned from 100 kHz to 0.1 Hz whereas for Si2, the perturbation amplitude was 10 mV and the frequency range was scanned from 200 kHz to 0.01 Hz.

Fig. 1. Galvanostatic curve of the first cycle of Si1 (full line) and Si2 (dashed line) at C/20.

A table summarizing the experimental conditions for Si1 and Si2 is reported in ESI.

3. Results and discussion

3.1. Electrochemical signatures

Even though the two studied silicon electrodes are made of comparable materials, they differ in some distinct ways. Si1 has a smaller average diameter, larger surface area and thicker native oxide layer than Si2. Fig. 1 shows the galvanostatic curve of cycle 1 of both electrodes, Si1 and Si2. Both galvanostatic curves show comparable features. Indeed, Si1 and Si2 present a plateau during lithiation around 0.10V. The fully lithiated capacity for Si1 is 3 850 mAh.g⁻¹, compared to 3 800 mAh.g⁻¹ for Si2. Both recorded values exceed the theoretical capacity for silicon of 3 579 mAh.g⁻¹. This can be easily explained by the additional consumption of electrons to form the SEI layer at the surface of the electrode [26]. Actually, Si1 only reaches a coulombic efficiency of 83%, whereas Si2 reaches 92%. The difference in coulombic efficiency can be explained by the larger production of SEI, possibly due to a larger surface area and thicker oxide layer, which makes the surface of Si1 more chemically reactive [27].

To identify undoubtedly the different phenomena as Charge Transfer (CT) or SEI, which can be observed by EIS, several impedance spectra were recorded along representative cycles. Since the very first electrochemical cycle, which results in a complete amorphization of the active material, is very specific for Si-based electrodes [14,28], these measurements were actually carried out upon the second electrochemical cycle and/or subsequent cycles, since it has already been shown that nano silicon-based electrodes are stable from the 2nd to the 50th cycle, in standard cycling conditions [16].

Fig. 2 compares both the galvanostatic curves of cycle 2 as well as the evolution of the impedance spectra for Si1 and Si2. Even though both electrodes differ in active material, electrode composition, and surface area, the shape of the impedance signals is comparable. All the spectra show two semi-circles at High Frequencies (HF), i.e. f > 1 Hz and straight lines in the Low Frequencies (LF) region, i.e. f < 1 Hz. The HF region is typical of interfacial phenomena: the two semi circles observed for our system, in that domain, can be associated with the presence of the SEI at the electrode surface and the charge transfer (CT) process. The characteristic frequency associated with the first HF semi-circle remains constant upon cycling (~50 kHz for both Si1 and Si2) suggesting that this semi-circle corresponds to a passivation surface layer and is here related to the SEI, of which the composition is almost not dependent on the state of charge of the electrode [15,16]. The characteristic frequency of
the second HF semi-circle evolves with the voltage: for both Si1 and Si2 it varies from 300 to 1 500 Hz. thus, we can attribute this second semi-circle to the CT process. The straight lines, in LF region, can be easily related to the Li-diffusion processes in the Si bulk active material. However, in addition to these relatively standard and already observed semi-circles, the EIS spectra systematically exhibit, for both systems, an inductive loop at lower potentials. As far as we know, this kind of inductive phenomenon has never been reported in the literature for silicon electrodes. Moreover, as the experimental conditions for Si1 and Si2 are completely different, it is very hard to believe that the presence of this loop comes from an instrumental artefact. On both recordings, we can see that this inductive loop is always observed below 0.35 V vs Li. Additionally, **Fig. 3** shows the impedance spectra, obtained with different perturbation signals: 5, 10, 20 and 30 mV. Changing the excitation amplitude has a direct influence on the inductive part of the spectrum, since the different curves are not superimposable at these medium frequencies. Conversely, we note that the HF and LF part of the different spectra are similar, indicating that the change in perturbation amplitude only has an influence on the inductive part. Consequently, the inductive phenomenon is surely a parasitic reaction, intrinsic to the electrochemical system under investigation.

An inductive loop has rarely been reported for EIS spectra in the LIB research field. Two main hypotheses are proposed in the literature to explain this particular phenomenon: (i) a phase change of the active material during the measurement or (ii) heterogeneity of the lithium distribution inside the electrode which creates concentration cells between the different particles. Since the lithiation and delithiation of silicon in cycle 2 are of a solid solution type [28,29], the first hypothesis can hardly explain the inductive loop and can consequently be eliminated. However, in addition to the last hypothesis, it is also known that the SEI layer on the surface of silicon electrodes is very unstable and continuously consumes electrons and lithium ions. It is thus possible for this process to change the current flowing through the system during the EIS measurement, causing an electromotive force superimposed to the lithium intercalation and potentially explaining the inductive loop [30].

In the following, several complementary experiments have been performed on both Si1 and Si2 systems to discriminate between the most probable hypotheses: heterogeneity of the lithiation or instability of the SEI layer.

### 3.2. Influence of the C-rate

If the inductive loop in the impedance spectra, present at lower potential states, is caused by heterogeneity in the lithiation, altering the cycling rate should have an influence on the presence of the inductive phenomena. Since a slower lithiation favors the homogeneity of the lithiation, the disappearance or, at least, a decrease of the phenomenon is expected. On the other hand, if the inductive loop is caused by instability of the SEI layer, changing the...
cycling rate should only have a minimal effect. To illustrate this, the impedance spectrum of a cell with a slower cycling rate (C/50) was recorded, using a Si1 electrode. Fig. 4 shows the spectrum at fully lithiated state in cycle 2. The inductive effect is still clearly present on the spectrum, suggesting its source does not depend on the cycling rate. This first experiment is rather in favor of certain instability of the SEI layer.

3.3. Influence of the temperature

The temperature is one of the key parameters for an impedance measurement, since it has a great influence on the viscosity of the electrolyte, the ionic conductivity and the electrochemical kinetics processes [31]. Multiple measurements at different temperatures were performed on a quasi-steady state Si2 electrode, after 6 charge-discharge cycles (Fig. 5). The equilibrium potential before measurement was 0.302 V vs Li, which corresponds to a capacity of 1 200 mAh.g⁻¹. The first measurement was performed at a temperature of 25 °C. The cell was then heated to 50 °C and afterwards cooled again to 25 °C and further to 0 °C. Afterwards it was heated again to 25 °C.

After heating to 50 °C, the global impedance of the system decreases. The higher temperature improves both the viscosity and the ionic conductivity of the electrolyte. Furthermore, the kinetics of the charge transfer and the diffusion in the active material are enhanced. On the other hand, the formation of SEI is also favored. Studies on graphite electrodes have indeed shown that elevated temperature increases the kinetics of electrolyte degradation [32,33]. Subsequently, since the high temperature increases both the ionic mobility (favoring homogeneity of the lithiation) and the formation of the SEI, it is difficult, at that stage, to conclude on the origin of the inductive loop which is still clearly present.

However, the second measurement at 25 °C, after heating at 50 °C, is not superimposable with the original spectrum, indicating that an irreversible phenomenon has occurred at 50 °C. Concerning the repartition of lithium in the silicon electrode: increasing the temperature has surely favored a more homogeneous distribution of lithium. Taking Fick’s law into account, it would be very surprising, that the lithium distribution will return to its possible heterogeneous state after lowering the temperature. If the heterogeneity of the lithiation is indeed at the origin of the inductive loop, the stay of the electrode at 50 °C would have caused the inductive phenomenon to now disappear or, at least, to decrease. Since the inductive loop has increased, the hypothesis of the instability of the SEI is more relevant. Moreover, the first HF semi-circle (related to the SEI layer) is bigger, suggesting again the electrolyte degradation is clearly activated at high temperature.

Furthermore, lowering the temperature to 0 °C results, as expected, in an increase of the total impedance, since the electrolyte viscosity increases whereas the ionic mobility in both the electrolyte and the active material decreases [34]. Note also the perfect superposition of the spectra recorded at 25 °C, before and after the stay at 0 °C indicating that no irreversible (electro)chemical process occurs at 0 °C (in contrast to what happens at 50 °C).

3.4. Influence of the electrolyte

The influence of the electrolyte on the inductive phenomenon in the impedance spectrum has also been investigated. Since the electrolyte mainly contributes to the composition of the SEI layer, it will also play an important role on its behavior during cycling. The influence of fluoroethylene carbonate (FEC) as an electrolyte additive was thus investigated here, since it is known to produce a smoother and more stable SEI layer [35–37].

Fig. 6 compares two impedance spectra, with and without FEC additive, at the 10th cycle, after a lithiation of 1 200 mAh.g⁻¹. The addition of FEC results in an increase of the characteristic frequency associated with the SEI, from 50 kHz to 100 kHz, indicating a noticeable modification of its chemical composition (change of the dielectric permittivity), in good agreement with XPS results obtained elsewhere [36]. Note also that the size of the inductive loop has decreased; the latter being related to the better stability of the SEI in presence of FEC. We can also observe a noticeable decrease of the potential at which the inductive loop now appears (< 0.2 V vs Li). This last statement, together with the decrease of the inductive effect observed in the EIS spectra, confirms that the SEI formation is both improved and stabilized in presence of FEC additive in the electrolyte.

Once again, these results confirm that the inductive phenomenon is more likely caused by the instability of the SEI at the surface of silicon particles.
3.5. Proposed (electro)chemical mechanism

The results from the three complementary aforementioned experiments indicate that the main origin of the inductive phenomenon on the impedance spectra is probably the instability of the SEI on the Si particle surface. During the impedance measurement, part of the electrons and Li\textsuperscript+ ions would be involved in the irreversible reaction of SEI formation. Fig. 7 shows a schematic representation of the mechanism for such a reaction at the silicon-electrode/electrolyte interface. The lithiation of silicon is an electro-insertion reaction, associated with the double layer charge together with the charge transfer process, which would be here in competition with the reduction of the electrolyte. To explain the appearance of possible inductive impedance, this reduction reaction shall contain a two-step process based on a Volmer-Heyrovsky-type reaction [38]. The first step is an adsorption of lithium ions together with reduction products of the electrolyte at the electrode surface. The second step is a combination of the latter adsorbed species to form the final SEI layer. The detailed equations and their mathematical treatments are attached in appendix. From the analytical resolution of these kinetic equations, an electrical equivalent circuit could be deduced to model the proposed mechanism and finally to fit the recorded impedance data. The HF part of the equivalent circuit (related to interfacial reactions) is shown in Fig. 8.

As already extensively described in literature [11,17,22,24,25,39], the high frequency part contains the resistance of the electrolyte (R\textsubscript{e}) and the R\textsubscript{SEI}/C\textsubscript{SEI} system corresponding to the impedance of the SEI deposit. The mid frequency part contains the double layer capacitance (C\textsubscript{dl}), the charge transfer resistance (R\textsubscript{ct}) and an R\textsubscript{SEI formation}/L\textsubscript{SEI formation} couple corresponding to the inductive loop, related to the SEI formation/deposition. Note also that the equivalent circuit in Fig. 8 was only used to model spectra containing the inductive loop. Obviously, for other spectra, R\textsubscript{SEI formation}/L\textsubscript{SEI formation} was left out.

One has to bear in mind that it is delicate to interpret the physical meaning of R and L individually. From their analytical expressions, both are linked to the formation process of the SEI layer. However, R\textsubscript{SEI formation} could be seen as the ease to form the SEI. The meaning of L\textsubscript{SEI formation} is slightly more delicate since it contains both contributions of the faradic current. Actually, the faradic current (I\textsubscript{f}), shown in Fig. 8, is divided between two processes: charge transfer (CT) and SEI building (passivation). If the contribution of SEI formation is small, I\textsubscript{f} will be determined by the CT resistance solely. Hence, no inductive loop will be observed. During the process of SEI formation, I\textsubscript{f} will also have a R\textsubscript{SEI formation}/L\textsubscript{SEI formation} contribution, resulting in the presence of an inductive loop, at mid frequencies, in the impedance spectrum. For example, Table 1 presents the potential at which an inductive loop appears for Si2 in cycle 2. As already mentioned, the inductive phenomenon only appears at low potentials. Consequently, the process of SEI formation, and accordingly the adsorption of lithium ions, takes place at low potentials on silicon electrodes. According to literature, with graphite electrodes the decomposition of electrolyte and formation of SEI occurs at higher potentials, generally between 1 V and 0.5 V vs Li and separated from the lithiation of the electrode. Literature also described this to be the case for silicon electrodes [17,40–42]. Different values for the potential range have been reported, but generally the SEI formation takes place between 1.5 V and 0.25 V vs Li, after which lithiation occurs between 0.25 V and 0 V vs Li.

The results presented in this paper indicate that both processes (SEI formation and lithiation of the silicon electrode) do take place simultaneously at low potentials. One can probably argue that during the SEI formation between 1.5 V and 0.25 V vs Li, as no–or little–lithiation occurs, the volume of Si particles do not change, whereas, during the lithiation process (between 0.25 V and 0 V vs Li), the volume of the particles increases markedly, increasing the surface of the Si particles which induces a second SEI formation.
Table 1

Values of the parameters obtained for the EIS spectra for cycle 2 of the Si2 electrode. At certain (higher) potentials RSEI formation and LSEI formation were not observed.

<table>
<thead>
<tr>
<th>Decreasing Potential (V)</th>
<th>0.40</th>
<th>0.38</th>
<th>0.33</th>
<th>0.31</th>
<th>0.29</th>
<th>0.25</th>
<th>0.22</th>
<th>0.20</th>
<th>0.19</th>
<th>0.17</th>
<th>0.12</th>
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</thead>
<tbody>
<tr>
<td>R0 ((\Omega)cm²)</td>
<td>9.3</td>
<td>8.7</td>
<td>8.4</td>
<td>8.5</td>
<td>7.7</td>
<td>8.2</td>
<td>8.4</td>
<td>8.5</td>
<td>8.8</td>
<td>8.7</td>
<td>8.8</td>
</tr>
<tr>
<td>RSEI ((\Omega)cm²)</td>
<td>5.5</td>
<td>3.1</td>
<td>1.2</td>
<td>1.1</td>
<td>0.96</td>
<td>1.0</td>
<td>1.1</td>
<td>1.4</td>
<td>2.2</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Rct ((\Omega)cm²)</td>
<td>6.6</td>
<td>4.5</td>
<td>3.3</td>
<td>3.4</td>
<td>1.8</td>
<td>1.5</td>
<td>1.4</td>
<td>1.7</td>
<td>2.8</td>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>RSEI formation ((\Omega)cm²)</td>
<td>-</td>
<td>-</td>
<td>0.234</td>
<td>0.6</td>
<td>0.9</td>
<td>1.2</td>
<td>1.32</td>
<td>1.6</td>
<td>2.4</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>LSEI formation ((\Omega)cm²)</td>
<td>-</td>
<td>-</td>
<td>4.7\times10^{-4}</td>
<td>1.3\times10^{-3}</td>
<td>1.6\times10^{-3}</td>
<td>1.9\times10^{-3}</td>
<td>2.3\times10^{-3}</td>
<td>2.4\times10^{-3}</td>
<td>3.1\times10^{-3}</td>
<td>5.6\times10^{-3}</td>
<td>1.1\times10^{-2}</td>
</tr>
<tr>
<td>Increasing Potential (V)</td>
<td>0.2</td>
<td>0.23</td>
<td>0.26</td>
<td>0.28</td>
<td>0.31</td>
<td>0.34</td>
<td>0.38</td>
<td>0.40</td>
<td>0.43</td>
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<td>(upon delithiation)</td>
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<td></td>
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</tr>
<tr>
<td>R0 ((\Omega)cm²)</td>
<td>8.8</td>
<td>10</td>
<td>9.2</td>
<td>8.6</td>
<td>8.8</td>
<td>9.9</td>
<td>8.9</td>
<td>9.2</td>
<td>8.8</td>
<td>8.9</td>
<td>9.1</td>
</tr>
<tr>
<td>RSEI ((\Omega)cm²)</td>
<td>2.8</td>
<td>2.6</td>
<td>1.9</td>
<td>1.4</td>
<td>1.3</td>
<td>1.4</td>
<td>3.1</td>
<td>4.6</td>
<td>6.6</td>
<td>5.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Rct ((\Omega)cm²)</td>
<td>7.8</td>
<td>6.6</td>
<td>4.3</td>
<td>3.2</td>
<td>3.5</td>
<td>4.3</td>
<td>4.5</td>
<td>5.6</td>
<td>5.8</td>
<td>7.2</td>
<td>7.8</td>
</tr>
<tr>
<td>RSEI formation ((\Omega)cm²)</td>
<td>1.5</td>
<td>1.3</td>
<td>0.9</td>
<td>0.7</td>
<td>0.44</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSEI formation ((\Omega)cm²)</td>
<td>1.9\times10^{-3}</td>
<td>2.6\times10^{-3}</td>
<td>1.4\times10^{-3}</td>
<td>9.8\times10^{-4}</td>
<td>7.2\times10^{-4}</td>
<td>3.2\times10^{-4}</td>
<td></td>
<td></td>
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</table>

![Fig. 9. Experimental and modelled spectra obtained during cycle 2 after a lithiation of 2 400 mAh.g⁻¹ and a potential of 0.21V.](image)

4. Conclusion

The electrochemical impedance study, performed on the second electrochemical cycle, on two distinct nano silicon-based materials with 2 different 3-electrodes cell configurations, has allowed identifying the different characteristic frequencies associated to:

(i) the presence of the SEI layer on the surface of the silicon particles around 50 kHz;
(ii) the charge transfer process between 300 and 1 500 Hz (varying with the working potential)

This work has also highlighted the presence, below a specific voltage (depending of the electrolyte composition), of an inductive loop: a particular phenomenon, rarely observed in the field of Li-ion batteries, and to the best of our knowledge, never mentioned for silicon-based electrodes. Several complementary and independent experiments, performed on both nano Si-based systems, suggest that it is mostly the instability of the SEI on the surface of the silicon particles that causes the appearance of the inductive loop on the corresponding EIS spectra. Finally, a reaction mechanism and an equivalent electrical circuit, associated to this phenomenon, are proposed to model this effect. As a conclusion, it clearly appears here that the EIS technique is particularly interesting to study the stability/coverage of the SEI on the surface of silicon electrodes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2014.06.069.

References


Further reading
