Influence of the Molecular Weight of Poly-Acrylic Acid Binder on Performance of Si-Alloy/Graphite Composite Anodes for Lithium-Ion Batteries

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In this study Si-alloy/graphite composite electrodes are manufactured using water-soluble poly-acrylic acid (PAA) binder of different molecular weights (250, 450 and 1250 kgmol⁻¹). The study aims to assess the behavior of the different binders across all the steps needed for electrodes preparation and on their influence on the electrodes electrochemical behavior. At first, rheological properties of the water-based slurries containing Si-alloy, graphite, conductive carbon and PAA are studied. After coating, the adhesion strength and electronic conductivity of the manufactured electrodes are evaluated and compared. Finally, the electrochemical behavior of the composite anodes is evaluated. The electrodes show high gravimetric as well as high areal capacity (~ 750 mAh/g; ~ 3 mAh/cm²). The influence of the binder on the first cycle irreversible loss is considered as well as its effectiveness in minimizing the electrode volume variation upon lithiation/de-lithiation. It is finally demonstrated that the use of 8 wt.% of PAA-250k in the electrode formulation leads to the best performance in terms of high rate performance and long term stability.

Introduction

The necessity to meet the global energy demands has motivated researchers to focus more on alternative and sustainable energy sources. Going toward renewable energies will require the development of effective energy storage devices in order to cope with the intermittent nature of renewable sources. In this energy revolution Li-ion batteries are likely to play a central role as it is already happening for the storage of electricity produced by solar panels in private habitations. Furthermore, electric vehicles are considered as the next viable option as they are less polluting and sustainable. The growing e-mobility market requires high energy density LIBs at reduced price.

Graphite is the most successful anodes for LIBs but its capacity is comparatively low (372 mAhg⁻¹). Silicon, and more in general Li-alloying materials, has drawn research attention due to its high theoretical capacity (3578 mAhg⁻¹), abundance and comparatively low working potential (0.4 V vs. Li).[1—6] With a gravimetric capacity ten times higher than that of conventional graphite anodes, silicon has the potential to become the replacement for graphite. Although silicon has a high theoretical capacity, it often shows low first cycle coulombic efficiency and very large volume expansion upon full lithiation.[3] At room temperature, the Li–Si alloying process can bring up to the formation of crystalline Li₅Si₄. The de-lithiation of such a phase proceeds with a two phase mechanism with the end member having large difference in term of molar volume. This would eventually lead to particle and electrode pulverization because of too high stress at the interphase.[7] One other key aspect is that the expansion breaks the solid electrolyte interphase (SEI) at the particles level and exposes new surface to the electrolyte, thus leading to thickening of the SEI and consequent loss of available lithium.[2] At the cell level, the high expansion can cause cell bulging, separator failure and therefore safety concerns.

In this work an attempt of improving the electrochemical performance of Si-alloy/Graphite anodes through the optimization of the binder agent is presented. The usage of durable polymeric binder such as Poly Acrylic Acid (PAA) and other water soluble binders enables to maintain the contact between particles and substrate even after several tens of cycles.[2,8—12] The PAA binder is a water-soluble polymer which is easy to handle and enables organic solvent-free electrode preparation. PAA contains carboxylic groups that undergo condensation reaction with hydroxides/oxides groups of Si surface and forms secondary bonds.[13] Ideally, it covers the alloy particles uniformly and the interface between electrode/electrolyte is modified by the polyacrylate layer which acts like an artificial SEI layer. It therefore reduces the area of active material directly exposed to the electrolyte and hinders the ICL.[2,14,15] The linear PAA polymers are partly cross-linked by the hydrogen bonding which allows elastic deformation without breaking the polymer network and also holds the fractured particles in contact. PAA also shows higher adhesion strength towards copper foil due to the interaction of its carboxylic moieties with copper oxides on copper surface.[11,15,16]

In the present work, PAA is used to manufacture Si-alloy/Graphite composite electrodes with areal capacity of 1250 kg mol⁻¹.
Results and Discussion

3.1 Slurry and electrode development

The development of high quality, stable electrode slurries containing the active and inactive components is a non-trivial process. However, this process is often overlooked. Rheological properties as well as sedimentation behavior are in fact rarely considered at the lab scale, although they play a key role when electrodes for LIBs have to be produced at larger scale. As reported elsewhere,\(^\text{[17]}\) the use of the PAA binder helps avoiding sedimentation as it acts as dispersant agent. Independently from the molecular weight of the PAA being used, all slurries designed, developed and reported hereafter showed no sedimentation. Even after prolonged resting time (unstirred up to 72 h), no phase separation (solid/liquid) has been indeed observed. Looking at the rheological properties of the water-based slurry, flow curves indicate how the viscosity of the slurry changes under the different shear rates. Irrespective of the molecular weight of the binders, all slurries showed a non-Newtonian and a shear-thinning behavior (Figure 1) due to the breakdown of polymer network structure when the shear rate is increased.\(^\text{[19]}\) As expected, the increase in molecular weight of PAA determines an increased slurry viscosity. That is particularly evident at low shear rates where the 250k has the lowest viscosity and the 1250k the highest. Despite the low solid content of the slurry containing PAA-1250k (Table 1), its very high viscosity made difficult the handling and therefore it was discarded from further analysis. Reducing further the solid content is not a viable option as it would require coating electrodes with a too high wet thickness in order to reach the targeted areal capacities.

Worth to mention that we aimed at producing electrodes with comparatively high areal capacity (~3 mAh/cm\(^2\)). Finally, it is noted that the viscosity of the slurry containing 4 wt.% PAA 250k is similar to that containing 8 wt.% PAA 250k.

The thixotropic behavior of the slurry was evaluated by using 3-interval time test. Initially low shear rate was applied, which simulates the slow mixing in the vessel.\(^\text{[19]}\) At such slow shear rate all slurries showed relatively constant viscosity (some increase due to water evaporation could not be prevented). A high stress was then applied for a short interval of time, which resembles the shear applied during the casting process. At high shear rate, all the slurries decrease their viscosity. After that the shear rate was decreased and the slurry was allowed to recover to its steady state. Figure 2 demonstrates that both 4 and 8 wt.% 250k slurries showed good relaxation characteristics and rapidly attained steady state viscosities. This non-Newtonian behavior is advantageous in electrode processing. A low viscosity slurry is indeed required for good coating at high shear rate conditions, whereas a high viscosity medium can prevent or minimize particle sedimentation when the slurry is at rest or during drying.

![Figure 1. Flow curve of the water-based slurries containing PAAs of different MWs and concentration.](image1)

![Figure 2. Results of 3-ITT for different electrode slurries](image2)

Table 1. Overview of solid content in the processed slurries

| S. No. | Material     | solid content (%) |
|-------|--------------|------------------|
| 1.    | 8 wt.% 250k  | 54.71            |
| 2.    | 8 wt.% 450k  | 40.72            |
| 3.    | 8 wt.% 1250k | 22.28            |
| 4.    | 4 wt.% 250k  | 56.34            |

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To be noted that the 8 wt.% 450k did not reach the steady state value within 250s and that the increase in viscosity after 200s for 4 wt.% 250k can be attributed to the drying up of solvents.\[20\]

After coating, the mechanical properties of the electrode tapes were investigated. More precisely, the adhesion (coating-to-current collector) strength was evaluated. Adhesion strength is a relevant parameter for electrodes for Li-ion batteries, particularly for those affected by high degree of volume variation during charge/discharge, as those based on silicon. The mechanisms through which the PAA binds the particles to each other and to the current collector can be explained considering its interaction with copper oxides of the current collector and with the native oxide layer which is found on the surface of the silicon particles.\[13\] Electrodes containing 8 wt.% of PAA-250k and PAA-450k have showed remarkably higher adhesion strength than those containing 4 wt.% PAA-250k (Figure 3).

3.2 Electrochemical characterization

First cycle lithium loss affects all anodes that work outside the stability window of the electrolyte and is due to the formation of the so-called Solid Electrolyte Interphase (SEI). Si, Si-alloys and Si/Graphite composites are no exceptions as their working potential is well below 1 V vs. Li. Nevertheless, minimizing the lithium losses is of primary importance in view of full cell performance where the only source of lithium is the cathode. Irreversible lithium loss would in fact reduce the amount of usable lithium and therefore decrease the cell capacity and energy. In half-cells against Li metal this issue has much lower impact as the availability of Li-ion is virtually unlimited. We recently\[21\] introduced a term called Efficient Capacity (Ceff) defined by the formula reported below, and that takes into account both the irreversible and reversible capacity of a given anode material.

\[
C_{\text{eff}} = \frac{Cc}{C_e + C_i}
\]

In the formula Ce represents the reversible capacity of the anode, Ci the irreversible capacity of the anode, and Cp the reversible capacity of the cathode. We considered Cp as 170 mAh/g, a reasonable capacity for a Li[Ni1/3Co1/3Mn1/3]O2 cathode at moderate C-rates. The first cycle efficiency of the Sialloy/ graphite composite anodes presented in this paper remained almost unaffected by the selection of the binder and found to be in the range of 86–87%. The efficient capacity was found of ~437 mAh/g, about 1.6 times higher than that of graphite (267 mAh/g).

During the first lithiation, the Li–Si alloying and Li-Graphite intercalation processes lead to a variation of the electrode thickness and volume. By setting as starting value the thickness of the electrodes at the fresh state, we derived the increase in thickness after the first lithiation. As it is shown in Figure 4 the electrode containing PAA-450k under-

| S. No. | Material | Electronic Conductivity (S.cm\(^{-1}\)) |
|-------|----------|----------------------------------------|
| 1.    | 8wt.% 250k | 0.056                                  |
| 2.    | 8wt.% 450k | 0.049                                  |
| 3.    | 4wt.% 250k | 0.121                                  |

Figure 3. Adhesion strength of electrodes manufactured with PAA binders of different MWs and concentration

Table 2. Electronic conductivity of electrodes manufactured with different PAA-binders and different concentration

Figure 4. Swelling behavior of the manufactured electrodes and dependence on the selection of the binder.
goes an expansion of 105 %, which is lower than that of electrodes containing PAA-250k in concentration of 8 wt.% and 4 wt.% (117 % and 123 %, respectively).

Upon de-lithiation the electrodes shrunk although they did not regain the original thickness. A certain amount of volume change remains even after complete de-lithiation, which is termed as irreversible volume change in Figure 4, and assessed at about 40 % for all the electrodes. The thickness of the electrode was also measured after rate capability tests (electrochemical results shown in Figure 5 and Figure 6). Both electrodes containing 8 wt.% of binder (either 250k or 450k) showed very similar values and increased their thickness by about 55 %. The higher volume change for the electrodes containing 4 wt.% PAA-250k points out that the binder concentration is not sufficient to reduce/prevent the silicon volume expansion. The poor mechanical stability of...
the electrode was already demonstrated during the peeling test and now found to remarkably affect the swelling behavior.

The rate performances of the Si-alloy/graphite electrodes are showed in Figure 5.

One advantage of using Si-alloy in the electrode formulation is that it helps reducing the weight and thickness of the electrode. In fact, if same areal capacities (expressed in mAh/cm²) and porosities are considered, a Si-containing electrode would have remarkably lower thickness than that of a graphite-based one. Transport properties would therefore be faster and rate capability might also be boosted. Beside these general considerations, Figure 5 demonstrates that the rate capability of electrodes containing 8 wt.% PAA-250k are much better than that of electrodes comprising 4 wt.% PAA-250k and 8 wt.% PAA-450k. Of note is that even at 3 C electrodes were able to retain more than 90% of their low-rate capacity. All galvanostatic de-lithiation profiles (Figure 6) collected at low C-rates show the classical plateaus of the lithium de-intercalation from graphite at potentials below 0.25 V vs Li.

At higher potentials only a sloped curve is visible which is characteristic for the de-alloying of lithium from amorphous silicon. Figure 5 also demonstrates that the lower concentration binder is clearly the worst performing. Even at low current rates the achieved capacities are lower than for the other electrode formulations. That poor electrochemical behavior is attributed to the poor adhesions/cohesion strength that reduces particle-to-particle contact and eventually leads to the mechanical failure of the electrode. Electrodes containing PAA-250k and PAA-450k at concentration level of 8 wt.% show rather similar performance at low currents. However, the PAA-450k is not able to achieve the same performance of the PAA-250k as higher overpotential affects the former electrodes when the current load increases (Figure 5 and Figure 6). Such evidence can be explained considering the lower measured electronic conductivity at the electrode level (Table 2). Moreover, higher molecular weight of the binder might result in a larger coverage of the active material particles, which increases the adhesion capability (in agreement with results of Figure 3) but slows down the ionic mobility in the electrode, as suggested by Lee et. al. and Kovalenko et. al.

Endurance tests (Figure 7a) demonstrate that electrodes containing 8 wt.% 250k and 450k have nearly identical capacity retention after 150 cycles. There is in fact a difference of -1% in the retained capacity after 150 cycles. On the other hand, there is a drastic reduction of the capacity delivered by the electrodes with 4 wt.% 250k binder. Figure 7b depicts the evolution of the coulombic efficiency as function of the cycle number. The average coulombic efficiency for 8 wt.% PAA-250k binder material (~99.89) is higher than the 8wt.% 450k binder material (~99.73). But the coulombic efficiency is lowest for the 4 wt.% PAA-250k (~99.67) and we suggest that this is due to its inability in preventing the electrode expansion thus increasing the lithium loss associated with SEI re-formation.

### 3.3 Post-mortem SEM analysis

SEM micrographs of pristine electrodes (Figure 8 a–c) demonstrate a uniform and comparable morphology for all electrodes, regardless of the binder molecular weight and concentration. On the other hand, the morphological analysis of the electrodes after the endurance tests shows remarkable differences. At first we noted a clear increase in surface roughness and development of microcracks. This effect was particularly evident in 8 wt.% PAA-450k electrode with the development of significantly large crack on the surface. The electrode containing 4 wt.% PAA-250k binder had very high surface roughness. Moreover, due to its poor mechanical stability some parts of the active coating peeled off during the cell opening steps. On the other hand, the post-mortem investigation on electrodes containing 8wt.% of PAA-250k binder electrodes showed the least signs of aging, in good agreement with the electrochemical results, which demonstrated the best long term stability and rate capability among all the binders used.
**Conclusions**

The study herein presented tries to shed light on the effects of the molecular weight and concentration of poly-acrylic acid binder on the processability and electrochemical behavior of Si-alloy/graphite composite electrodes for lithium-ion batteries. Three different molecular weights of the PAA binder were selected (250, 450 and 1250 kg mol\(^{-1}\)), whereas the concentration was changed between 4 and 8 wt.%. We have found PAA-250k at concentration of 8 wt.% to be the best performing binder. It guaranteed excellent slurry processability, rheological behavior as well as very high adhesion of the electrode layer to the Cu current collector. Furthermore, the selected binder achieved the best electrochemical performance in terms of rate capability (90 % of capacity retention at 3 C) and cycling stability (86 % capacity retention after 150 cycles).

**Experimental Section**

2.1 Binder preparation

The binder aqueous solution was prepared for 450k and 1250k whereas PAA-250k was already available as a solution. PAA binder powder of 450k, 1250k (Sigma-Aldrich Co. LLC.) and deionized water were mixed at 400 rpm at room temperature for 3 hours in a mixer (DISPERMAT). Since the PAA is acidic in nature, a 3 M LiOH solution was added to neutralize the solution (pH 7.5). Several stirring times were evaluated before selecting 3 h as our “standard” procedure. No differences in terms of rheological behaviour of the slurries as well as adhesion strength and electronic conductivity of the electrodes could be observed. It was therefore concluded that 3 h were enough to fully dissolve the binder.
2.2 Anode preparation

The dry powders including Si-alloy (3 M, Germany), graphite (SMG-A3, Hitachi, Japan), Super-PLi (Imerys) were mixed in their dry state before the addition of binder solution. Table 3 shows the exact electrodes recipe. The deionized water was added under the viscosity. Then a momentary high stress for a period of 2000 N was applied during the measurement. The potential was linearly swept between the copper rods in the range (0 V–0.2 V) at a scan rate of 5 mV (VersaSTAT 4). The measurement was also taken without electrode to eliminate the contribution of system resistance. From the linear voltammetry curve the ohmic behaviour (VI curve) and conductivity was measured based on the geometry of the electrode.

2.3 Rheological investigation

Two different rheological tests were performed in order to understand the flow properties of the slurry using an Anton-Paar MCR 102 rheometer.

I. Steady state flow test which provides information about the flowability at different shear rates (0.01 s\(^{-1}\) to 1000 s\(^{-1}\)).

II. Stress relaxation test was performed to find out the thixotropic behaviour of the slurry. It has three steps involved. Initially, the slurry was stirred at a low shear rate to measure the viscosity. Then a momentary high stress for a period of ~1 s was applied to determine the breakdown of the structure. Finally, the slurry was allowed to reach recover and reach the steady state viscosity.

2.4 Adhesion strength testing

The adhesion/cohesion strength of electrodes was measured by using an adhesion strength testing machine (Zwick/Roell). The electrode was fixed between parallel plates using a double-sided adhesive tape (3 M). The area of the measurement surface was maintained as 6.45 cm\(^2\). A compression stress of 2000 N was applied for 60s to ensure proper adhesion of the tape to the electrode surface. The pull off phase (1000 mm/min) was initiated and the maximum tensile force was measured during the failure.

2.5 Electronic conductivity

The electronic conductivity of the electrodes was measured by placing the electrode (Ø 12 mm) in the probe of the conductivity cell between two copper rods. A constant pressure of 0.9kN was applied during the measurement. The potential was linearly swept between the copper rods in the range (0 V–0.2 V) at a scan rate of 5 mV (VersaSTAT 4). The measurement was also taken without electrode to eliminate the contribution of system resistance. From the linear voltammetry curve the ohmic behaviour (VI curve) and conductivity was measured based on the geometry of the electrode.

2.6 Electrochemical tests

The electrochemical performance of Si-alloy composite electrodes with different MWs LiPAA binders were evaluated by galvanostatic cycling in half cells against lithium counter electrode. The cells were constructed in an argon glove box (H20 < 0.1 ppm O2 < 0.1 ppm) (mBraun) with electrolyte 1 M LiPF6 in EC:EMC 3:7 (BASF) + 10 wt. % FEC (UBE Europe) and glass fiber separators (GF-A,Whatman). Based on the type of experiment, the tests were carried out in 2-electrode coin cell (Hohsen CR2032) or 3-electrode (T-cell) using BaSyTec workstation (BaSyTec GmBH, Germany) or VMPs (Bio-Logic, France). The electrochemical measurements were performed in a potential window 0.005 V - 0.9 V with a formation cycle which includes CC–CV lithiation (0.1 C–0.025 C) and CC delithiation (0.1 C). The swelling of the electrodes was investigated by monitoring the changes in the thickness after its first lithiation and delithiation. In the rate capability test, the different delithiation current rates, from 0.1 C to 3 C, were applied while the lithiation step was unchanged with CC–CV (0.25–0.05). The cyclic stability was checked by continuous cycling CC–CV lithiation step (0.25–0.05) and delithiation step CC(0.025).

2.7 SEM investigation

The topography of cycled and fresh electrodes was analysed using SEM Leo Gemini 1530 VP microscope equipped with Gemini thermal field emission column. The topography of washed and dried electrodes using SE detector at accelerating voltage 5 kV reveals the surface information like cracks, pore distribution and surface roughness.

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Conflict of interest

The authors declare no conflict of interest.

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[1] W. J. Zhang, *J. Power Sources* 2011, 196, 13–24.

[2] M. N. Obrovac, V. L. Chevrier, *Chem. Rev.* 2014, 114, 11444–11502.

[3] B. Liang, Y. Liu, Y. Xu, *J. Power Sources* 2014, 267, 469–490.

[4] A. Birrozzi, R. Raccichini, F. Nobili, M. Marinaro, R. Tossici, R. Marassi, *Electrochim. Acta* 2014, 137, 228–234.

[5] F. Maroni, M. Marinaro, A. Birrozzi, G. Carbonari, R. Tossici, F. Croce, R. Marassi, F. Nobili, *J. Power Sources* 2014, 269, 873–882.

[6] B. P. N. Nguyen, S. Chazelle, M. Cerbelaud, W. Porcher, B. Lestriez, *J. Power Sources* 2014, 262, 112–122.

[7] K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel, *J. Electrochem. Soc.* 2010, 157, A1354—A1360.

[8] M. Marinaro, M. Weinberger, M. Wohlfahrt-Mehrens, *Electrochim. Acta* 2016, 206, 99–107.

[9] W. Porcher, S. Chazelle, A. Boulenceau, N. Mariage, J. P. Alper, T. Van Rompaye, J.-S. Bridel, C. Haon, *J. Electrochem. Soc.* 2017, 164, A3633—A3640.

[10] Z.-J. Han, N. Yabuuchi, K. Shimomura, M. Murase, H. Yui, S. Komaba, *Energy Environ. Sci.* 2012, 5, 9014.

[11] A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C. F. Huebner, T. F. Fuller, I. Luzinov, G. Yushin, *ACS Appl. Mater. Interfaces* 2010, 2, 3004–3010.

[12] G. Gabrielli, M. Marinaro, M. Mancini, P. Axmann, M. Wohlfahrt-Mehrens, *J. Power Sources* 2017, 351, DOI 10.1016/j.jpowsour.2017.03.051.

[13] D. Mazouzi, Z. Karkar, C. Reale Hernandez, P. Jimenez Manero, D. Guyomard, L. Roué, B. Lestriez, *J. Power Sources* 2015, 280, 533–549.

[14] S. Komaba, N. Yabuuchi, T. Ozeki, Z. J. Han, K. Shimomura, H. Yui, Y. Katayama, T. Miura, *J. Phys. Chem. C* 2012, 116, 1380–1389.

[15] D. Mazouzi, N. Delpuech, Y. Oumellal, M. Gauthier, M. Cerbelaud, J. Gaubicher, N. Dupré, P. Moreau, D. Guyomard, L. Roué, et al., *J. Power Sources* 2012, 220, 180–184.

[16] S. Komaba, K. Okushi, T. Ozeki, H. Yui, Y. Katayama, T. Miura, T. Saito, H. Groult, *Electrochem. Solid-State Lett.* 2009, 12, A107.

[17] M. Marinaro, D. Iwan Yoon, G. Gabrielli, P. Stegmaier, E. Figgemeier, P. C. Spurk, D. Nelis, G. Schmidt, J. Chauveau, P. Axmann, et al., *J. Power Sources* 2017, 357, 188–197.

[18] H. Y. Tran, M. Wohlfahrt-Mehrens, S. Dsoke, *J. Power Sources* 2017, 342, 301–312.

[19] M. Secchiarioli, S. Calcatera, H. Y. Tran, S. J. Rezvani, F. Nobili, R. Marassi, M. Wohlfahrt-Mehrens, S. Dsoke, *J. Electrochem. Soc.* 2017, 164, A672—A683.

[20] J. Mewis, N. J. Wagner, *Adv. Colloid Interface Sci.* 2009, 147–148, 214–227.

[21] D. Guy, B. Lestriez, R. Bouchet, D. Guyomard, *J. Electrochem. Soc.* 2006, 153, A679.

[22] B.-R. Lee, E.-S. Oh, *J. Phys. Chem. C* 2013, 117, 4404–4409.

[23] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, *Science (80-. ).* 2011, 334, 75–79.

[24] G. W. Lee, J. H. Ryu, W. Han, K. H. Ahn, S. M. Oh, *J. Power Sources* 2010, 195, 6049–6054.

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