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Performance-Determining Factors for Si–Graphite Electrode Evaluation: The Role of Mass Loading and Amount of Electrolyte Additive

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The mass loading of Si–graphite electrodes is often considered as a parameter of secondary importance when testing their electrochemical performance. However, if a sacrificial additive is present in the electrolyte to improve the electrochemical performance, the electrode loading becomes the battery cycle-life-determining factor. The correlation between mass-loading, electrolyte additive, and binder type was investigated by analyzing the cycling behavior of Si–graphite electrodes, prepared with water-based binders, with mass loading ranging from 3 to 9.5 mg cm⁻² and cycled with FEC electrolyte additive, while keeping electrolyte amount constant. A lower loading was obtained by keeping slurry preparation steps unchanged from binder to binder and resulted in a longer lifetime for some of the binders. When the final loading was kept constant instead, the performance became independent of the binder used. Since such results can lead to the misinterpretation of the influence of electrode components on the cycling stability (and to a preference of one binder over another in our case), we propose that a comparison of long-term electrochemical performance data of Si–graphite electrodes needs to be always collected by using the same mass-loading with the constant electrolyte and additive.

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The increasing market demand for Li-ion batteries (LIBs) is leading researchers all over the world to develop simple but feasible approaches to improve gravimetric and volumetric energy of commercial cells. One of the approaches to reach such a goal is by increasing the specific charge of the negative electrode. The simplest method to do so is to mix graphite ($Q_{th} = 372 \text{ mAh g}^{-1}$) with a specific charge-enhancing component (i.e., an element or compound possessing a significantly higher specific charge than graphite), such as silicon ($Q_{th} = 3572 \text{ mAh g}^{-1}$). Even though on one hand, such a composite electrode thus created provides higher specific charge; on the other hand, Si-based electrodes suffer poorer cycling stability due to Si volume changes during alloying with Li.^{1–3} Volume changes result, among others, in cracks in the solid electrolyte interphase (SEI) layer, which leads to a continuous consumption of the electrolyte at the electrode surface and gradual loss of electronic contact between electroactive material particles and conductive carbon.^{4,5}

An improvement in cycling stability can be obtained by preparing electrodes with preferably water-processable binders, such as poly acrylic acid (PAA), sodium carboxymethyl cellulose (Na–CMC), and Na-alginate, because they are able to partially buffer Si volume expansion thanks to the formation of a cross-linking network and a strong interaction with Si particles.^{6–11} Furthermore, the addition of additives to the electrolyte has been shown to improve the cycle life of alloy-based electrodes.^{12–17} Additives such as fluoroethylene carbonate (FEC) are able to form a thinner, homogeneous, and more mechanically stable SEI^{18–24} than the SEI formed in common carbonate electrolyte.

The long-term cycling stability of Si–graphite electrodes in presence of additives indirectly depends on another important parameter: the electrode mass loading. Because the additives are

often of the sacrificial character and are consumed during cycling, it has been proven that the lifetime of a cell, containing Si electrodes, is linearly dependent on the ratio between the additive and active material loading.¹⁴ This means that larger amount of additive or lower mass loading will result in a higher number of cycles with the same amount of electrolyte. Moreover, it should be considered that the amount of electrolyte in research cells is much higher than in commercial ones, and therefore same concentration of additive in electrolyte will result in significantly different absolute amount of additive available for interface protection, and the additive amount to active material loading are much more important. However, the electrode loading is a parameter very often overlooked in many scientific publications. Literature reports show no loading^{6,25–28} or, even more often, electrodes containing Si or Si–graphite are reported with a very broad range of loading values (1 to 10 mg cm⁻² considering the total amount of electroactive material or 0.1–2.5 mg cm⁻² considering only Si amount).^{5,29–35} There is two approaches how to perform comparable experiments: either keep the procedure constant or keep the final testing set up constant, — in this case, either slurry recipe or mass loading of final electrode. Alternative approach would be to adjust electrolyte and additive amount to the loading, which case experiment reliability is less robust.

Therefore, the goal of our study is to demonstrate the interrelation between electrolyte additive, electrode loading, and type of binder, and how these parameters influence the cycling stability of Si–graphite electrodes. In addition, we would like to make the battery community aware about the necessity of a standard performance comparison for Si–graphite electrodes, which has to take into account both the amount of additive used and the loading of the electrode.

Experimental

Materials.—The following materials were used for the electrodes preparation: Si nanoparticles (30–50 nm, 98%, Amorphous and Nanostructured Materials), C-ENERGY KS6L graphite ($d_{90} = 6.5 \mu\text{m}$, $S_{BET} = 18 \text{ m}^2 \text{ g}^{-1}$, Imerys Graphite & Carbon), C-ENERGY SuperC45 conductive carbon (SC45, average particle size = 37 nm, $S_{BET} = 45 \text{ m}^2 \text{ g}^{-1}$ ³⁶), binder mixture of polyacrylic acid (PAA, 25 wt% sol. in H₂O, average M.W. 240,000, Alfa Aesar) and carboxymethyl

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cellulose (CMC, Alfa Aesar) 1:1, binder mixture of CMC and styrene butadiene rubber (SBR, MTI corporation) 1:1, Guar Gum binder (Sigma-Aldrich), Na-alginate binder (Sigma-Aldrich).

Electrode preparation.—Electrodes were prepared with a weight ratio of active and inactive components (graphite: Si: SuperC45 carbon: binder) of 90:5:1:4.

In a standard preparation, the binder was initially dissolved in the solvent (a mixture of water:ethanol 70:30 wt% was used in case of PAA:CMC, CMC:SBR, and Na-Alginate, while only water was used in case of Guar Gum), then SC45 conductive additive and Si nanoparticles were stirred into the binder solution. Afterwards, graphite powder was added to the mixture and the slurry was stirred until a honey-like texture was obtained. The stirring was performed by turbo-stirrer (IKA Ultra-Turrax T25). After 2 h of degassing on a roller-mixer, the slurries were cast onto copper foil using the doctor-blade technique. The obtained electrode sheets were dried under vacuum at 80 °C overnight for all binders, with additional pre-treatment for PAA:CMC binder at 150 °C for 2 h, as at this temperature this binder mixture undergoes cross-linking.⁷ Circular electrodes of 13 mm diameter were punched out and re-dried overnight at 120 °C under vacuum to remove any remaining traces of water.

Electrochemical characterization.—The electrodes were assembled in Ar-filled glove-box (<0.1 ppm H₂O and <0.1 ppm O₂) into coin-type cells with metallic lithium ($\geq 99.9\%$, thickness 0.75 mm, Alfa Aesar) as a counter electrode and a glass fiber separator. The following electrolyte was used in this study: 1 M LiPF₆ in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1) (LP30, BASF) + 2 wt. of fluoroethylene carbonate (FEC) (BASF).

The ratios of FEC and electroactive material (EAM = graphite + Si) were calculated by dividing the molar amount of FEC in the electrolyte (expressed in μmol) by the mass of electroactive material in the electrode (in mg), respectively. The electrochemical measurements were carried out with a battery cycler (Astrol Electronics AG, Switzerland) at 25 °C with the cycling procedure applied as follows: the first constant-current (CC) cycle was performed at slow rate (20 mA g⁻¹) to allow the formation of the SEI, while further CC cycles were performed at 50 mA g⁻¹ for the lithiation, and at 186 mA g⁻¹ for the delithiation. After each CC step, the cut-off potential (5 mV for lithiation; 1.5 V for delithiation) was maintained until the current dropped below 5 mA g⁻¹ (constant-voltage (CV) step). In this study, the potential is referred vs Li⁺/Li and the specific charge is presented per mass of electroactive material, i.e., the sum of graphite and Si masses. To ensure reproducibility, for each given set of conditions, the cycling data of at least two nominally identical cells was taken into account. For presentation clarity, only the specific charge obtained on delithiation is shown in the performance graphs. A summary of the investigated electrodes along with the nomenclature used in the paper is presented in Table I.

Results and Discussion

Si-graphite electrodes with KS6L graphite, Si nanoparticles, PAA:CMC binder and a loading of around 9.5 mg cm⁻¹ cycled with a CCCV protocol in LP30 + 2 wt% FEC electrolyte are taken as a baseline in this study. Such a choice derives from the extensive research carried out by our group in the last few years on this type of electrodes; specifically, the type of silicon,³⁷ the cycling protocol,³⁸ and the electrodes' composition (i.e., the silicon amount and the graphite type) were optimized^{39,40} to maximize the electrochemical performance. In an attempt to improve even further the cycling stability, electrodes with different water-processable binders were produced (Table I), tested, and compared with the baseline.

The potential profiles for the 1st cycle are shown in Fig. 1a, while the electrochemical performance is shown in Figs. 1b and 1c and summarized in Table II.

For all investigated electrodes with different types of binder, the potential profiles show the characteristic reduction of FEC at around

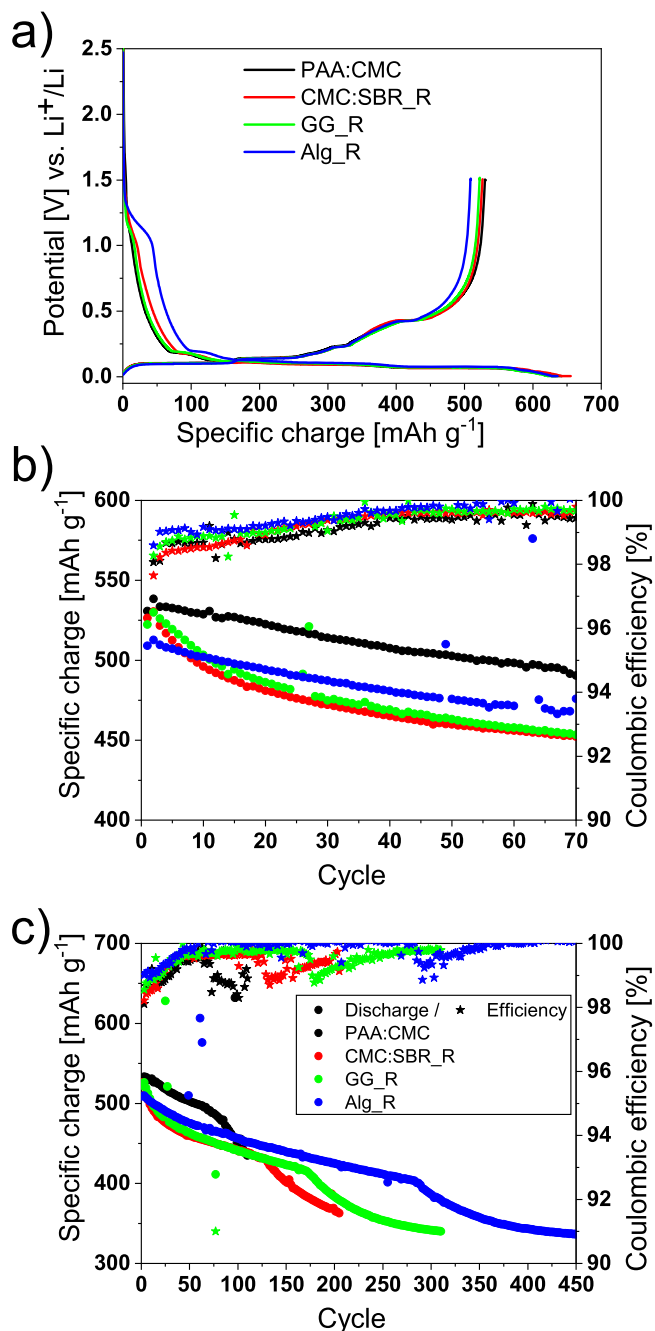


Figure 1. (a) Potential profile for the 1st cycle, (b) short-term and (c) long-term electrochemical performance of PAA:CMC (black), CMC:SBR_R (red), GG_R (green), and Alg_R (blue).

1.2 V during the first lithiation. As the lithiation proceeds, the plateaus, related to the alloying of Li with Si, and the intercalation of Li into graphite, are visible below 0.3 V. During the 1st delithiation, the three plateaus associated with graphite are visible up to 0.25 V and then, at 0.45 V, the plateau related to the delithiation of crystalline Li₁₅Si₄ phase is clearly distinguishable. Interestingly, the potential profile in the proximity of FEC reduction potential differs slightly depending on the binder composition. The differences can be better seen in the differential capacity plots (Fig. S1). The noticeable reduction of FEC starts earlier at a higher potential for CMC:SBR_R and Alg_R electrodes, specifically at around 1.35–1.4 V; while it starts around 1.15–1.2 V for PAA:CMC_R and GG_R electrodes. Furthermore, electrodes with Na-Alginate binder show a much more pronounced FEC reduction, hence a

Table I. An overview of the investigated electrodes. The electrode composition was always graphite:Si:SC45:binder = 90:5:1:4. R and U stand for “regular” and “unified” loadings, respectively.

Name	Binder (total 4%)	Average loading ± 0.5 (mgEAM cm ⁻²)	Solid content (%)	Blade gap (μm)	Average thickness ± 2 (μm)	Average density ± 0.02 (g/cm ³)	Estimated porosity ± 1 (%)
PAA:CMC	2 wt% PAA:2 wt% CMC	9.8	31	250	165	0.62	72
CMC:SBR_R	2 wt% CMC:2 wt% SBR	7.1	27	250	130	0.57	74
GG_R	4 wt% Guar Gum	5.4	23	250	90	0.64	71
Alg_R	4 wt% Na-alginate	3.7	17	250	70	0.55	75
CMC:SBR_U	2 wt% CMC: 2 wt% SBR	9.3	27	400	155	0.63	71
GG_U	4 wt% Guar gum	9.7	23	450	160	0.63	71
Alg_U	4 wt% Na-alginate	9.2	23	470	165	0.58	73

*The average values were calculated considering at least six electrodes.

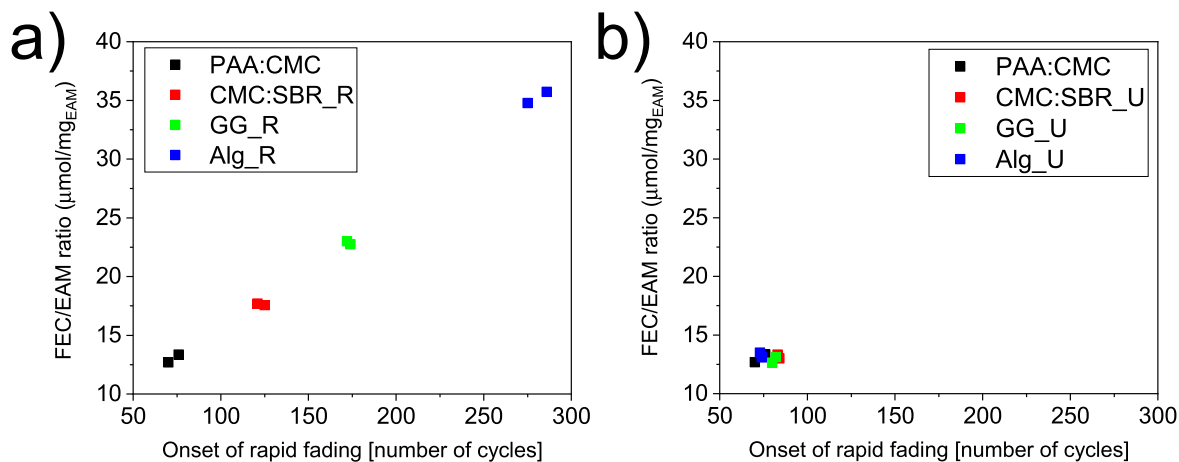


Figure 2. FEC/EAM ratio versus onset of rapid fading plots for a) regular electrodes and b) unified electrodes of PAA:CMC (black), CMC:SBR_R (red), GG_R (green) and Alg_R (blue).

higher irreversible specific charge associated to SEI formation in comparison with the other binders. The 1st cycle columbic efficiency is around 80%–82% for PAA: CMC, CMC:SBR and GG, while below 80% for Na-alginate. The higher reactivity of FEC towards alginate-based electrode might be explained by poorer alginate binder coverage of Si particles, and therefore higher electroactive area for FEC reduction, while the higher potential for FEC decomposition onset is most likely because of the higher decomposed FEC amount, which makes detection already at higher potentials possible. The first signs of FEC reduction have been shown as early as at 1.5 V.⁴¹

PAA:CMC electrodes provide a specific charge of around 540 mAh g^{-1} at the end of the 2nd delithiation, which is the highest among the electrode with studied binders and is also very close to the theoretical one of 540.8 mAh g^{-1} . Alg_R shows the lowest specific charge on the first discharge (512 mAh g^{-1}) indicating that roughly 15% of the Si nanoparticles are not participating to the reaction already from the initial cycles, which points to the poorer binder distribution and Si domains, inaccessible to either electrolyte or electrons. CMC:SBR_R and GG_R show a specific charge of around 530 mAh g^{-1} .

The cycling behavior of the electrodes was analyzed in the short (70 cycles, Fig. 1b) and long-term (450 cycles, Fig. 1c). During the first 70 cycles, both PAA:CMC and Alg_R electrodes fade with a nearly constant slope reaching a specific charge retention of 91%. CMC:SBR_R and GG_R electrodes instead show a rapid specific charge drop for the first 10 cycles, and successively the fading continues with a constant slope in the same way as electrodes with PAA:CMC and Na–Alginate binder. We hypothesize that the rapid fading might be the result of a different kind of interaction between Si particles and these two binders, as they lack the carboxyl groups, which have been shown to have a positive effect on cycling

stability.⁴² Indeed, guar gum and SBR do not have carboxyl groups and absence or reduction of carboxylic groups might be the reason for adversely affected initial cycling stability. The specific charge retention after 70 cycles is around 85% for electrodes with CMC: SBR and GG binder.

On the long term, all electrodes show a very similar behavior: a constant fading for a certain number of cycles, then a rapid fading known to be caused by the depletion of FEC, which is accompanied by a decrease in columbic efficiency.¹⁴ After the rapid fading, the specific charge converges to contribution of only graphite, showing that almost all of Si is by now inactive and presumably disconnected due to the surrounding SEI layer from the electronic conductive network. Ultimately, most of the cells completely fade either because of a short circuit caused by dendrite formation at the lithium counter electrode⁴³ or because the electrolyte consumption (Fig. S2).

Electrodes with Na-alginate binder seem to provide the best specific charge retention reaching 65% after 450 cycles, while electrodes with other binders are not even able to reach such a high cycle numbers. Even though at a first glance it seems that a straightforward conclusion is that Na–Alginate is the best binder for Si–graphite electrodes, we took it with caution due to difference in active materials loading, as from our previous studies, we have seen that experimental parameters can have a significant influence on the final performance of the cell.⁴⁴

As a first attempt to clarify if the loading has effect on cycle life and capacity retention, while using the same amount of electrolyte, and thus additive, we have plotted in Fig. 2 a ratio between the FEC amount and the electrode loading vs the cycle number corresponding to the onset of rapid fading (i.e., the last cycle before the columbic efficiency significantly drops). The result showed that the two parameters (i.e., the FEC/EAM ratio and the onset of rapid fading)

Table II. Electrochemical data of the investigated electrodes.

Name	Specific charge, mAh g^{-1} (Capacity retention, %)				
	2nd delithiation	70	200	300	450
PAA:CMC_R	538	490 (91)	0	0	0
CMC:SBR_R	530	453 (85)	366 (69)	0	0
GG_R	530	453 (85)	383 (72)	342 (65)	0
Alg_R	512	468 (91)	425 (83)	387 (75)	336 (66)
CMC:SBR_U	526	463 (88)	0	0	0
GG_U	530	456 (86)	0	0	0
Alg_U	533	482 (90)	0	0	0

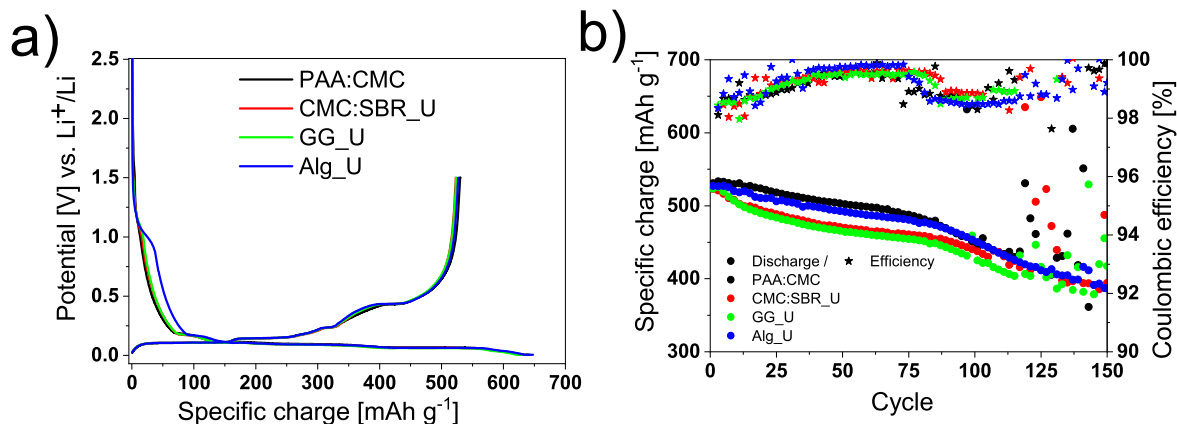


Figure 3. (a) potential profile for the 1st cycle and (b) electrochemical performance of PAA:CMC (black), CMC:SBR_U (red), GG_U (green) and Alg_U (blue).

are linked via a linear correlation: the higher active mass loading, the shorter is the cell's lifetime, and that this correlation is independent of the type of the binder. A linear correlation was already reported for Si electrodes cycled with different amounts of an electrolyte additive¹⁴ but our finding explain interrelation between electroactive materials loading, additive/electrolyte amount, and the type of binder. Based on this we can conclude that our results were the consequence of a clear and implicit trend: only the electrode loading and the electrolyte additive amount are decisive, while the electrochemical cycling results are independent of the binder used.

To experimentally verify our conclusion, all electrodes, earlier prepared using our standard procedure with different binders, while having different loadings, now were prepared adjusting the electrode preparation procedure to give comparable loadings to our baseline one (around 9.5 mg cm^{-2}). The potential profiles for the 1st cycle are shown in Fig. 3a and the electrochemical performance in Fig. 3b. The higher loading, obviously, does not change the potential profile of the electrodes, however a slight difference regarding FEC reduction is observed for Alg_U electrodes in comparison to lower-loading Alg_R electrodes. The higher loading shifts the signature of FEC reduction by ca. 0.1 V towards lower potentials (Fig. S3). The same effect was reported for Si electrodes prepared with only PAA or only CMC binders by increasing Si loading 2.5 times.⁴⁵ In our study, even though the Si amount was increased also 2.5 times, this effect was observed only with Na-Alginate. CMC: SBR_U and GG_U electrodes, show a specific charge after the 2nd delithiation of around 530 mAh g^{-1} , very close to that one of the lower loading electrodes with the same types of binder. However, electrodes with Na-Alginate show an improvement in specific charge reaching 533 mAh g^{-1} . The lower amount of solvent (i.e., higher solid content) necessary to obtain a higher loading resulted in a more homogeneous binder and carbon distribution in the electrode,⁴⁶ as well as a better connectivity between EAM and SC45 particles.⁴⁷ This leads to a higher amount of Si being exploited and resulted in a higher specific charge.

As for the cycling stability, high loading electrodes mimic the behavior of lower-loading electrodes in the initial 70 cycles. Alg_U shows a constant fading over cycling, while CMC:SBR_U and GG_U show a rapid drop during the initial 10 cycles, and then the specific charge drops in a constant fashion.

The pronounced difference in specific charge retention between electrodes with different binders (as shown in Fig. 1) is not observed when electrodes have all the same mass loading. High loading electrodes have nearly the same fading rates, independently of the type of the binder. The specific charge retention after 70 cycles is around 90%–91% for electrodes with PAA:CMC and Na-Alginate binders, and around 86%–88% for CMC:SBR and GG binders (Table II).

The complete consumption of FEC occurs at about the same number of cycles for all electrodes with ca. 9 mg cm^{-2} loading, i.e.,

after 70–80 cycles. The rapid fading after FEC consumption leads to a specific charge of around $380\text{--}390 \text{ mAh g}^{-1}$ after ca. 150 cycles and ultimately to complete cell failure after ca. 200 cycles for all binders (Fig. S4). The relationship between FEC/EAM ratio and rapid fading is visualized in Fig. 2a. It is now clear that, for Si-graphite electrodes, Na-Alginate is not a better performing binder than PAA:CMC but the additive amount and the loading are the two factors determining the cell lifetime.

Thus, it is obvious that the electrode loading plays an important role in the evaluation of electrochemical performance when electrolyte additives are used. A wrong interpretation of electrochemical data from electrodes with different loadings can actually disguise the importance of underlying experimental parameters. As an example, in Ref. 48, the low capacity retention of the electrodes with Na-Alginate was assigned to the binder but the fading is instead related to the complete consumption of the additive at a specific loading. Moreover, as FEC is the state-of-the-art electrolyte additive for Si-graphite electrodes in both research and industry, and more and more scientific publications report electrochemical performance with the use of this electrolyte additives, the care should be taken to unify the testing parameter. We believe that an objective comparison of long-term electrochemical performance between Si-graphite electrodes can only be done by using the same amount of electrolyte additive and comparative loadings.





Conclusions

The results of this study show that in presence of constant amount of electrolyte additive, the loading plays a major role in determining the cell cycle-life. Electrodes with various mass loadings and different types of binder were fading after a number of cycles, linearly correlating to additive/loading ratio and, contrary to the expectations, the battery cycle life did not depend on the type of binder. In the case, when electrodes were prepared with different binder types but with very close values for active materials loading, the differences in cycle life were minor, which leads to conclusion that the FEC consumption per amount of active material per cycle is the same, independently of binder used. This means that revisiting past results, where binder properties as performance-enhancing factors are considered using sacrificial additives, the careful scrutiny of experimental conditions and especially differences in electrode loading and electrolyte (additive) to active materials ratio should be done. Our results also show that in order to test effects of electrode composition changes (such as binder in our case), the same active material loading should be the guiding parameter and not the same electrode preparation conditions.

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