



On the origin of the capacity fading for aluminium negative electrodes in Li-ion batteries



Gabriel Oltean ^a, Cheuk-Wai Tai ^b, Kristina Edström ^a, Leif Nyholm ^{a,*}

^a Department of Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-75121, Uppsala, Sweden

^b Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691, Stockholm, Sweden

HIGHLIGHTS

- The capacity loss for aluminium nanorod anodes is due to lithium trapping.
- The capacity loss is controlled by the diffusion of lithium in the aluminium.
- Very good cycling stability was seen between 0.1 and 1 V vs. Li⁺/Li.
- The cycling performance was not affected by the alumina layer thickness.
- Volume expansion effects do not explain the cycling behaviour.

ARTICLE INFO

Article history:

Received 25 April 2014

Received in revised form

9 June 2014

Accepted 22 June 2014

Available online 7 July 2014

Keywords:

Aluminium

Nanorods

Li-ion battery anode

Capacity loss

Diffusion

Volume expansion

ABSTRACT

The origin of the capacity loss for aluminium negative electrodes in Li-ion batteries has been studied for electrodeposited aluminium nanorod electrodes coated with Al₂O₃ layers of different thicknesses (i.e. a native oxide layer, 30 and 60 nm) mainly employing pouch cell voltammetric cycling versus metallic lithium. Whereas the capacity decreased continuously during cycling between 0.1 and 3 V vs. Li⁺/Li, good cycling stability was obtained when the cycling was carried out between 0.1 and 1 V vs. Li⁺/Li. Since no significant dependence of the cycling stability on the thickness of the alumina layer was found in any of the experiments, the observed loss of capacity is unlikely to have been caused by volume expansion effects. The latter is further supported by the finding that the capacity (obtained when cycling between 0.1 and 3 V vs. Li⁺/Li) decreased linearly with the inverse of the square root of the cycling time, indicating that the capacity loss was due to the loss of lithium as a result of lithium diffusion into the bulk of the aluminium electrodes. The latter is explained based on a lithium-aluminium alloying and dealloying model which complements previously published models.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Aluminium is widely used as the positive electrode current collector in Li-ion batteries since it is corrosion resistant, light and relatively inexpensive. As aluminium forms an alloy with lithium at a potential close 0 V vs. Li⁺/Li, aluminium could in principle also be used as a negative electrode material [1]. This would facilitate the manufacturing of Li-ion batteries significantly as aluminium then could be used both as the positive current collector and as a combined negative current collector and electrode. At present, significant research efforts are made to enable a replacement of the commercially employed graphite negative electrode material with

higher capacity metals or metal oxides [2]. In this quest, silicon and tin have received a lot of attention since they can form alloys with up to 4.4 Li atoms per metal atom and therefore provide high gravimetric as well as volumetric specific capacities. During the alloying and dealloying with lithium, Si and Sn electrodes, however, experience significant volume changes of the order of 300–400% which generally give rise to capacity losses upon cycling. In analogy with silicon and tin, aluminium also forms alloys with lithium although the reaction in this case generally is assumed to involve only one lithium atom per aluminium atom, yielding a theoretical capacity of about 1000 mAh g⁻¹ and a volume expansion of less than 100%.

The use of aluminium as a negative electrode material in Li-ion cells, however, suffers from poor coulombic efficiencies and rapid capacity fading upon cycling. This capacity fading, which generally is most pronounced during the first few cycles, is currently mainly

* Corresponding author. Tel.: +46 (0)184713742; fax: +46 (0)18513548.

E-mail address: leif.nyholm@kemi.uu.se (L. Nyholm).

ascribed to volume expansion effects although the experimental support for this conclusion is less convincing for aluminium than for silicon and tin, at least for electrodes of conventional dimensions. Conflicting conclusions regarding the origin of the capacity loss for aluminium negative electrodes during cycling can also be found in the literature, particularly when comparing contemporary and older publications.

In attempts to investigate the capacity loss upon cycling, aluminium negative electrodes have been studied by many groups [3–29] employing different electrode preparation and characterisation approaches during more than four decades. The influence of particle size [3–5], crystal orientation [6] and electrode morphology [7] on the cycling performance of aluminium electrodes have thus been studied but the results are unfortunately contradictory. The use of an inactive component in the aluminium matrix [8,9] or a buffer layer [10] covering the aluminium particles have likewise been investigated without significant success.

The performance of aluminium nanorod or nanowire negative electrodes in Li-ion batteries has also been studied by several groups [11–13]. Zein El Abedin et al. [11] synthesised aluminium nanowires which were cycled for 50 cycles and which showed no significant capacity loss during the first four cycles in contrary to other published results [12,13]. Recently, Liu et al. [14] described an *in situ* TEM study of aluminium nanowires indicating that the aluminium alloying and dealloying processes give rise to isolated aluminium nanoparticles underneath the native alumina oxide layer even though the structural integrity of the nanowire was maintained. Based on the latter results it is tempting to conclude that the capacity losses seen for aluminium electrodes mainly stem from a loss of electrical contact to parts of the electrode as a result of the stress caused by the volume changes as for silicon and tin electrodes.

Even though volume expansion effects may limit the cycling stability of aluminium electrodes, an examination of the older literature clearly shows that the cycling stability of aluminium electrodes is affected by at least one other effect since the cycling ability also has been reported to be limited by a loss of lithium in the aluminium electrode [15–29]. This poor capacity retention of aluminium electrodes has been ascribed to lithium trapping in the aluminium electrode during cycling [15–17]. It has, however, also been found that aluminium electrodes can be efficiently cycled provided that a certain degree of alloying of the aluminium electrodes is achieved and that only about 2% of the capacity is used in the cycling [18,19]. The cycling efficiency of the aluminium negative electrodes has likewise been found to depend on the current density, the cycled charge [20] and the pretreatment of the electrodes [21]. Although Li_3Al_2 and Li_9Al_4 alloys were expected to form during lithiation of the aluminium electrode [15,16], only the LiAl phase was observed experimentally using X-Ray diffraction [22]. The nucleation and 3-D growth process involved in the formation of the alloy between aluminium and lithium has also been studied in detail [23].

Three decades ago, Owen and co-workers [24,25] proposed a model in which a growing layer of β -LiAl is formed on aluminium electrodes during the lithiation process while the delithiation reaction gives rise to a trapped β -LiAl layer between two lithium deficient layers. In this model, a lower diffusion coefficient for lithium in the Li poorer α -LiAl phase ($10^{-11} \text{ cm}^2 \text{ s}^{-1}$ [26]) than in the β -LiAl phase (10^{-8} – $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ [27,28]) was used to explain the fact that coulombic efficiencies significantly below 100% generally were obtained on the first cycles. More recently, Ui et al. [29] studied the concentration profiles of lithium within aluminium electrodes and demonstrated that lithium was indeed present within the electrodes even after the dealloying step. The latter authors also showed that the lithiation and delithiation charge for

an aluminium electrode increased with the cycle number in cyclic voltammetry experiments in the potential region between 0 and 2.4 V vs. Li^+/Li .

At present there are consequently two main hypotheses regarding the origin of the capacity losses seen for aluminium negative electrodes in Li-ion batteries. Although the discussion at present mainly is focused on volume expansion effects, losses of lithium in the aluminium electrode should clearly also be taken into consideration which is why there is thus a need for studies in which the cycling performance of aluminium electrodes is evaluated based on these two hypotheses. Another issue that so far has received very little attention is the influence of the native alumina layer on the performance of aluminium electrodes in Li-ion batteries. Although it is known that thin alumina layers can be used to minimize the effects of volume changes for alloying electrodes [30,31], the effect of such layers on the cycling stability of aluminium electrodes has not been investigated systematically. If the capacity loss of aluminium electrodes is indeed due to volume expansion effects it would be anticipated that these problems could be circumvented by the use of aluminium electrodes coated with sufficiently thick alumina layers.

In the present work, the cycling performance of aluminium nanorod electrodes covered with a native layer of alumina, as well as with 30 nm and 60 nm thick alumina layers, respectively are discussed. The obtained dependence of the capacity on the cycle number is examined on the basis of the volume expansion and lithium loss hypotheses mainly employing cyclic voltammetric data obtained in different potential windows. Based on the obtained results, a model for the alloying and dealloying processes for aluminium electrodes is proposed which complements the previous models presented by Owen and co-workers [24,25].

2. Experimental

The aluminium rod electrodes were manufactured by galvanostatic electrodeposition of aluminium in the pores of a commercial polycarbonate (PC) membrane (Cyclopore, Whatman). The working and counter electrodes used in the electrodeposition step consisted of 500 μm thick aluminium plates (Goodfellow 99.999%) with 1 cm^2 areas. The working electrode, covered by a 200 nm pore size PC membrane (Cyclopore, Whatman), a glass fibre separator (Whatman) and the counter electrode were clamped together and immersed in an ionic liquid electrolyte consisting of 1-ethyl-3-methylimidazolium chloride (Alfa Aesar, >98%) and aluminium chloride (Alfa Aesar, 99.999%) in a 1:2 molar ratio. The galvanostatic deposition was carried out in an argon filled glove box (O_2 and $\text{H}_2\text{O} < 2 \text{ ppm}$) as has been described elsewhere [32]. At the end of the deposition, the PC membrane was dissolved in dichloromethane (Sigma–Aldrich, 99.8%) for at least 30 min, resulting in self-supported aluminium rods on an aluminium substrate.

The 30 and 60 nm thick oxide layers were obtained by anodisation of the aluminium rod electrode employing a three-electrode cell, in which the Al nanorod electrode was used as the working electrode, a platinum coil served as the counter electrode and a Ag/AgCl electrode was used as the reference electrode. The anodisation, which was carried out in a 1 M KNO_3 (Merck, 99%) aqueous solution, was based on the number of cyclic voltammetric scans between 0 and +1 V vs. Ag/AgCl (at a scan rate of 1 mV s^{-1}) required to obtain the oxidation charges corresponding to the desired alumina layer thicknesses (i.e. 0.67 and 1.34C for 30 and 60 nm, respectively).

Li-ion cells were assembled in polymer laminated pouch cells inside an argon filled glove box with oxygen and water levels lower than 2 ppm. The aluminium nanorod working electrode and the combined counter and reference lithium electrode were separated

Download English Version:

<https://daneshyari.com/en/article/7736185>

Download Persian Version:

<https://daneshyari.com/article/7736185>

[Daneshyari.com](https://daneshyari.com)