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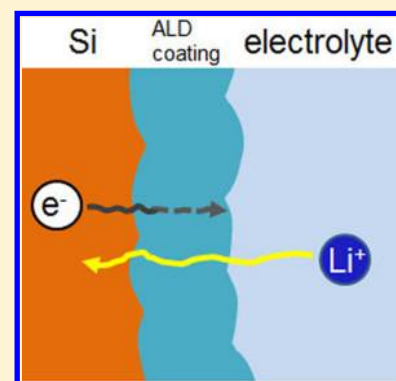
Atomic Layered Coating Enabling Ultrafast Surface Kinetics at Silicon Electrodes in Lithium Ion Batteries

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S Supporting Information

ABSTRACT: The interfacial charge-transfer kinetics plays an important role in the rate capabilities of lithium ion batteries (LIBs). The control of the charge-transfer kinetics, by engineering the surface coating so as to provide an artificial solid electrolyte interphase (SEI), can facilitate the lithiation/delithiation processes; however, unwanted interfacial resistance can be generated if the surface coating is too thick. Here, we provide an experimental study of the interfacial kinetics of a model LIB electrode system, silicon electrodes with alumina coatings by atomic layer deposition (ALD). A modified potentiostatic intermittent titration technique (PITT) is used to characterize the electrode operation and extract physicochemical parameters, including the lithium diffusion coefficient within silicon, the interfacial exchange current density, and the reaction rate constant. For the alumina–Si system, an optimum coating thickness exists in terms of delivering maximum charge-transfer rate. This work provides new tools to modify and improve key properties of engineered electrode/electrolyte interfaces.

SECTION: Energy Conversion and Storage; Energy and Charge Transport



The burgeoning market of renewable energy has increased the demand for advanced secondary energy storage media, especially lithium ion batteries (LIBs). Current LIB technologies do not meet the energy density, power density, and cycle life requirements for sustainable energy storage systems, especially hybrid and battery electric vehicles (HEVs and BEVs). LIB electrodes suffer from mechanical, chemical, and electrochemical degradations upon extended cycling. Nanostructured materials often deliver superior performance compared to their bulk counterparts^{1–8} because the nanostructure not only mitigates the mechanical degradation but also significantly enhances the power capability due to the shortened diffusion length. However, the high specific surface area of nanostructured materials can lead to the formation of a large amount of solid electrolyte interphase (SEI) film, which results in reduced capacity due to loss of lithium from the battery. Major efforts have been focused on stabilizing the SEI film or forming an artificial SEI to reduce the electrolyte decomposition and improve the capacity retention.^{9–14}

Surface modification of the electrodes, in particular, the application of surface coatings, has been employed to enhance the performance of both LIB anodes (negative electrodes) and cathodes (positive electrodes). Various transition-metal oxides and other ceramics, such as Al₂O₃, TiO₂, ZnO, MgO, and SnO₂, have been shown to be beneficial for the performance of LIB electrodes, especially for Si anodes.^{15–22} It is believed that engineered coatings can function as an artificial SEI, modify the surface chemistry of electrodes, act as a physical protection

layer on the electrodes, and scavenge (unwanted) hydrogen fluoride (HF).^{18,23}

The thickness of the coating or artificial SEI film is critical because it directly determines the electronic and ionic resistance. Ideally, the coating or artificial SEI should be thick enough to provide mechanical and chemical stability over the life of an electrode but thin enough so that significant ionic resistances are avoided. It has been reported that the metal oxide coating, such as Al₂O₃, reacts with the electrolyte and becomes a metal-oxy-fluoride or lithium-metal-oxide after cycling, which conducts lithium ions and blocks electrons.^{24–27} This fact brings more considerations into designing ideal coatings for LIB electrodes.

Here, we focus on understanding the interfacial kinetics of surface-coated electrodes in nonaqueous electrolyte systems. We chose Al₂O₃ (alumina) coatings on Si thin films; such an electrode system has a well-defined geometry and avoids complications associated with binders and conducting additives and thus provides information about the intrinsic properties of electrodes. The atomic layer deposition (ALD) technique is utilized to fabricate the coatings, which is a powerful tool to produce conformal, pinhole-free coatings with the ability to precisely control the thickness to the atomic layer scale.^{28–30} The charge-transfer kinetics of the Al₂O₃-coated Si electrodes

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was quantified using a modified potentiostatic titration technique (PITT).

We focus on the charging process of Si–Li half cells (delithiation process) because it is directly related to the utilization of the stored energy in full cells. Theoretical calculations show that the lithium insertion into a Si surface is the rate-limiting step; surface modification of the Si electrode could, therefore, be a promising approach to enhance surface kinetics.³¹ The reversible capacity of Si with different Al₂O₃ thicknesses, measured by galvanostatic cycling (C/10 rate), is shown in Figure 1. The reversible capacity of bare Si thin films

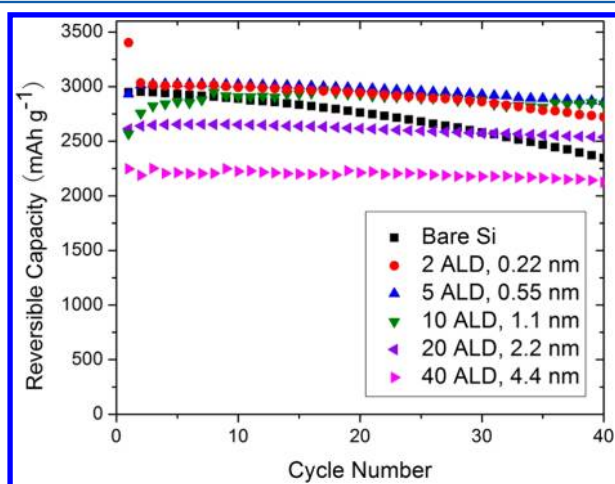


Figure 1. Reversible capacity of ALD Al₂O₃-coated Si thin films.

shows gradual decay upon extended cycling, 2953 mA h g⁻¹ in the second cycle and 2346 mA h g⁻¹ in the 40th cycle. The capacity decay from cycle 2 to cycle 40 corresponds to about 0.57% per cycle. ALD-fabricated Al₂O₃ coatings improve the reversible capacity retention of Si thin films significantly. For Si coated with two atomic layers of Al₂O₃, the average capacity loss from cycle 2 to cycle 40 is about 0.28% per cycle. Further increasing the ALD coating thickness to 10 or to 40 layers (1.1 to 4.4 nm) leads to gradual improvement of the capacity retention. The capacity loss from cycle 2 to cycle 40 is 0.11–0.13% per cycle for 10 and 40 layers, respectively. The Coulombic efficiency of Al₂O₃-coated Si and related discussion can be found in the Supporting Information. These results confirm that ALD-fabricated Al₂O₃ coatings can protect Si anodes, providing a stable artificial SEI.

The differences in the initial reversible capacity for the samples with various thicknesses of ALD coatings are most likely due to polarization differences of the substantially insulating properties of Al₂O₃. It has been reported that Al₂O₃ reacts with Li⁺ and forms LiAlO₂²⁴ or Li_xAl₂O₃²⁷ after cycling, which substantially conducts lithium ions and blocks electrons. The ionic conductivity of LiAlO₂ is 3×10^{-5} S cm⁻¹,³² much smaller than that of the state-of-the-art liquid electrolyte. Thus, adding thick Al₂O₃ atomic layers (20–40 ALD) could increase the ionic and electronic resistance and thus increase polarization. Plots of the differential capacity versus voltage for the first cycle (C/10 rate) are compared and discussed in the Supporting Information.

Although it is expected that the top layer (about 1 nm thick) of Al₂O₃ converts to LiAlO₂ upon cycling, the details of the electrode surface and the overall electrolyte/electrode interface remain unknown. Here, we focus on the overall interfacial

kinetics. To understand quantitatively the effect of Al₂O₃ coatings on interfacial kinetics, in particular, the charge-transfer process, we employ the modified PITT. The current response due to a small (5 mV) constant-potential excitation source is considered; the system is controlled by both diffusion and interfacial charge-transfer processes. The detailed derivation of the theory and methods can be found in ref 33, and a summary of the technique is provided in the Supporting Information. No cracks, which could affect diffusion processes,^{34–36} were observed by scanning electron microscopy after the PITT measurements. The electrochemical Biot number *B* measured by the modified PITT can be viewed as the ratio of the solute (Li) diffusion resistance to that of the overall charge-transfer process.^{33,37} A large Biot number represents a system whose kinetics is limited by diffusion, whereas a small Biot number represents a system governed by the charge-transfer process.

Figure 2 shows the electrochemical Biot number *B* as a function of ALD Al₂O₃ coating thickness. The values of the

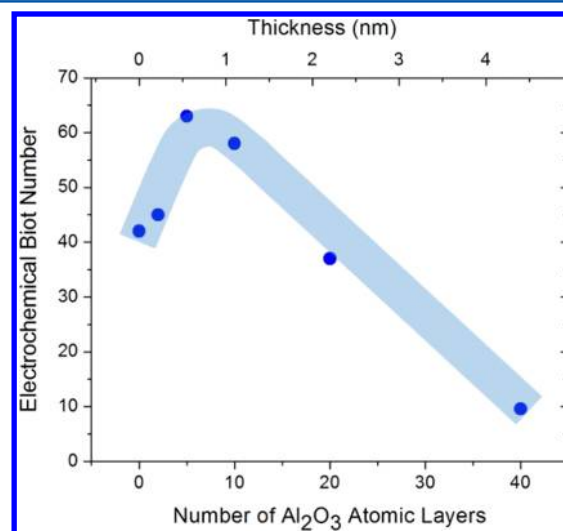


Figure 2. Electrochemical Biot number *B* obtained from PITT measurement. The light blue curve is provided to portray the trend in the data.

electrochemical Biot number can be divided into three regions. For pristine Si with natural SEI films formed in EC/DMC electrolytes, the electrochemical Biot number is about 42, representing a relatively facile interfacial kinetics. In other words, the process of lithium jump from the electrolyte to the electrode is faster compared to diffusion of Li in the Si electrodes. With up to 10 atomic layers of Al₂O₃ coatings (about 1.1 nm), the electrochemical Biot number increases and reaches a maximum value of between 56 and 63 when the coating is 5–10 layers thick. When the ALD Al₂O₃ coating is thicker than 20 layers, the electrochemical Biot number decreases sharply and is about 9 when the coating is 40 layers. The formation of SEI films is significantly suppressed by the Al₂O₃ coating, as well as the lithium ion conducting LiAlO₂ top layer.^{24,25} Thus, increasing of the electrochemical Biot number for 5–10 layers of Al₂O₃ is likely because of the formation of the an artificial SEI and suppression of the electrolyte decomposition. It is consistent with other observations that 10 layers of ALD Al₂O₃ coating provides improved rate performance of Cu–Si nanocable arrays³⁸ and that about 1 nm Al₂O₃ coating facilitates the charge-transfer process.³⁹ When the artificial SEI is thick, such as 20–40 atomic layers (2.2–4.4

nm), electrons transfer through this thick oxide layer would be much slower compared to the tunneling process through a thin oxide layer.^{25,40} As a result, for the case of thick coatings, the insulating nature of Al_2O_3 harms the kinetics and decreases the interfacial charge-transfer process, leading to decreased electrochemical Biot numbers.

Three other important electrochemical parameters, the Li diffusion coefficient in electrodes D , the exchange current density i_0 (see eq S4 (Supporting Information) for the definition), and the surface reaction rate constant k^0 (see eq S5 (Supporting Information) for the definition), can also be obtained from the modified PITT measurement. The Li diffusion coefficient in thin film Si measured in this work is about $1.2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, close to previously reported values.^{33,41,42} The exchange current density and surface reaction rate constant of Si coated with Al_2O_3 are summarized in Table 1, which have the same trend as the electrochemical Biot

Table 1. Exchange Current Densities and Rate Constants of ALD Al_2O_3 -Coated Si Measured from the Modified PITT

Al_2O_3 ALD atomic layers	exchange current density (mA cm^{-2})	reaction rate constant (cm s^{-1})
0	0.161	2.1×10^{-7}
2	0.172	2.2×10^{-7}
5	0.242	3.1×10^{-7}
10	0.223	2.9×10^{-7}
20	0.142	1.8×10^{-7}
40	0.037	4.8×10^{-8}

numbers. The procedure and parameters used to calculate the exchange current densities are provided in the Supporting Information.

When the magnitude of the current density is low, the electrochemical performance is governed primarily by the lithium diffusion, whereas both charge-transfer and diffusion resistances are important when the magnitude of the current density is high. Although the electrochemical Biot number in Figure 2 is only measured at a single lithium concentration during delithiation, it should represent the behavior of electrochemical delithiation processes semiquantitatively, especially at high rates. The delithiation capacity of Si with Al_2O_3 coatings at different rates is compared in Figure 3. To eliminate

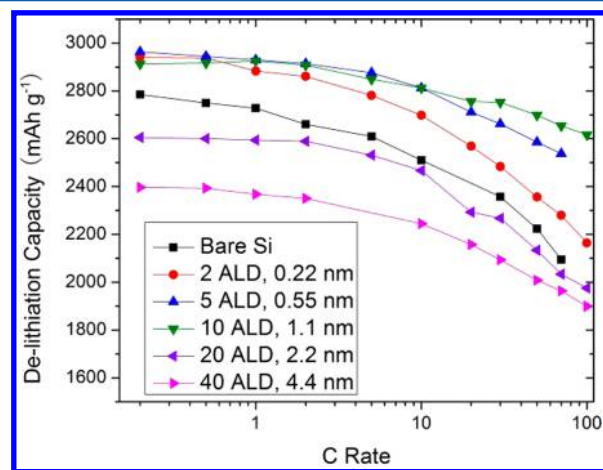


Figure 3. Reversible (delithiation) capacity of ALD Al_2O_3 -coated Si electrodes.

the effect of hysteresis, all samples were discharged at a slow rate of $C/20$ to 0.05 V before each measurement to ensure the same state of charge. It is shown that the capacity decreases for all samples with the increase of the charging C rate or current density due to kinetic resistance. Compared to pristine Si, two atomic layers of Al_2O_3 improves the delithiation capacity at high rates. The performance is the best for Al_2O_3 -coated Si with 5 and 10 ALD layers, both of which yield a lower overall interfacial resistance than that of pristine Si. Further increase of the coating thickness leads to a decay of delithiation capacity because of the associated increase in the overall charge-transfer resistance. For Si coated with Al_2O_3 , the optimal thickness for reducing the overall interfacial resistance is about 5–10 atomic layers of Al_2O_3 , or 0.55–1.1 nm. A recent work discovered that the optical thickness of ZnO coating on LiMn_2O_4 is six layers or 1.02 nm;⁴³ another work confirms that 0.5% of AlF_3 coating on a layered cathode gives the best performance.¹⁷ The results of cycling at various C rates (Figure 3) are consistent with the observed trend in the electrochemical Biot number displayed in Figure 2, indicating that the modified PITT³³ can be used to predict the performance of coated electrode materials.

An interesting phenomenon is that all samples in this work show generally good performance under high current density operation. For example, the delithiation capacity of 100 nm thick pristine Si under a rate of 70C is 2094 mA h g^{-1} , 75% of its capacity under a $C/5$ rate. The delithiation capacity of Si with 2 Al_2O_3 ALD coatings is 2164 mA h g^{-1} at a rate of 100C, 74% of its capacity at $C/5$. The delithiation capacity of Si with 10 Al_2O_3 ALD coatings (1.1 nm) is 2617 mA h g^{-1} at a rate of 100C, 89.8% of its capacity at $C/5$. A detailed comparison of the charging profiles of Si with two ALD coatings is shown in Figure 4. Voltage polarization is clearly seen in the profiles

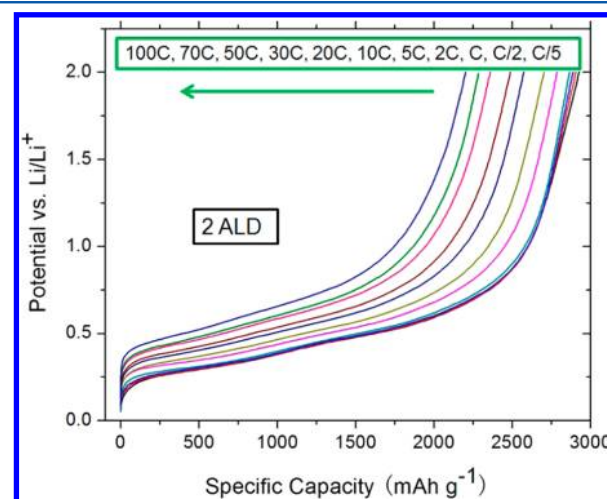


Figure 4. Delithiation potential capacity profiles of Si with two layers of ALD Al_2O_3 coating.

when the current increases. No obvious voltage capacity profile change due to damage of the electrode is observed. The characteristic time for diffusion of Li within the Si film corresponds to the square of the film thickness (100 nm) divided by the Li diffusion coefficient ($1.2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ when the Li concentration is equilibrated at 0.4 V versus a Li metal reference), or 833 s. Note that the 100C rate corresponds to a theoretical charging time of 36 s and practically only about 22 s; hence, it is understandable that not all of the Li can be extracted from the Si film. These observations do indicate that

well-designed and -engineered Si can have good intrinsic rate performance, which bodes well for high-energy LIBs employing Si or Si-enhanced anodes.

In summary, we studied the kinetics of Si thin film electrodes coated with Al_2O_3 by ALD using a model system of thin films that provides the intrinsic properties of electrodes. Using a modified PITT measurement, we quantify the overall interfacial resistance of ALD Al_2O_3 -coated Si electrodes and obtained exchange current density as a function of coating thickness. Three physicochemical parameters were extracted, including the lithium diffusion coefficient within silicon, the interfacial exchange current density, and the reaction rate constant. With 5–10 atomic layers of an alumina ALD coating, the thin film silicon electrode can deliver a 2600 mA h g^{-1} capacity within 24 s. We demonstrate that ALD surface coatings as artificial SEI layers can improve the cycle stability and facilitate the charge transfer at the Si electrode surface. The modified PITT can be applied to study other surface-modified electrodes for LIBs.

■ EXPERIMENTAL SECTION

Amorphous Si thin films (100 nm thick) were deposited on Cu current collectors by an E-beam evaporation system. Trimethylaluminum (TMA, Sigma-Aldrich) and high-performance liquid chromatography grade water (Sigma-Aldrich) were used as the precursors in the ALD system (Cambridge Nanotech) to deposit the Al_2O_3 coatings on the Si electrodes.⁴⁴ Al_2O_3 -coated Si electrodes were used as working electrodes, and pure Li foils were used as the counter electrodes in CR-2025 coin cells. One piece of a polypropylene separator (Celgard 3501) was used in each cell. The electrolyte was 1 M LiPF_6 dissolved in a solution of ethylene carbonate/dimethyl carbonate (Novolyte). Electrochemical measurements were tested using a multichannel potentiostat (VMP3, Bio-Logic). The upper and lower cutoff voltages of galvanostatic cycling are 2 and 0.05 V, respectively. The C rate is reported according to the theoretical capacity of Si; 1C corresponds to a current density of 4200 mA g^{-1} . Coin cells were cycled four times before each PITT measurement to minimize the intrusion of initial side reactions involved in the formation of a stable SEI. The PITT experiments were carried out around 0.4 V during charging of the half cells (delithiation of Si). The applied voltage step was 5 mV, and the cutoff current for PITT measurements was to 1 mA g^{-1} .

■ ASSOCIATED CONTENT

■ Supporting Information

The Coulombic efficiency and cycling profiles of Si– Al_2O_3 electrodes are discussed in the Supporting Information. Discussion of the modified PITT and an example of current response and the calculation of reaction rate constant are provided in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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