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Chemically stable artificial SEI for Li-ion battery electrodes

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The importance of coating’s chemical stability in lithium-ion batteries has been demonstrated by this study. It is well known that the mechanical properties determine the cycle life, and chemical stability or chemical degradation rate determines the calendar life. In this study, we used HfO2 coatings developed by atomic layer deposition as an example to show the chemical stability of the coatings for lithium ion battery electrodes. Published by AIP Publishing.

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Lithium ion batteries (LIBs) have been the choice of energy storage systems for portable electronic devices, uninterruptible power supplies, and electric vehicles. Exploring novel electrode materials with higher capacity, better rate capability, longer life, and lower cost is in urgent need for using LIBs in wider applications. For example, Si electrodes are able to deliver over 3600 mAh/g capacity, but the cycle life and calendar life are still too short due to both intrinsic issues of electrodes (such as large volume change) and surface chemical instability.1–6

Mechanical and chemical degradation are the two major degradation mechanisms of most LIBs. Usually, the cycle life is determined by the mechanical degradation rate and the calendar life is determined by the rate of chemical degradation. The stability of the electrode-electrolyte interphase, or solid-electrolyte interphase (SEI), in a non-aqueous electrolyte is critically important for stabilizing the electrodes and enabling the long-term cyclability.7–10 The stability of the SEI can significantly influence the life of LIBS. Intensive research efforts have been devoted to designing the SEI by incorporating electrolyte additives, such as FEC (Fluoroethylene Carbonate), VC (Vinylene Carbonate), and LiBOB (Lithium Bis(oxalato)borate).11–14 These electrolyte additives can help form stable SEIs on electrodes to prevent further decomposition of electrolytes. Even with the additives, however, the formation of the SEI is still a Li consuming process, which causes irreversible Li loss (or capacity loss) during the formation cycles. In addition to electrolyte additives, surface coatings or artificial SEIs (a-SEIs) have been employed to improve the functionalities of electrodes.15,16 There are many advantages of a-SEIs, such as reducing the irreversible capacity loss, improving the kinetics of electrodes, and better compositional control of SEI layers.17,18 The a-SEIs should be electronically insulating (suppress the electrolyte reduction), Li ion conducting, and chemically stable.7

Recently, several coatings made by atomic layer deposition (ALD) have been demonstrated to be effective a-SEIs to protect the electrodes. There are many advantages of ALD, such as the film was deposited under a relative low temperature with controllable thickness of atomic precision, accurate stoichiometry, and excellent uniformity and conformity.16,19–22 TiO2, Al2O3, ZnO2, SnO2, and SiO2 coatings are used as protection layers for both cathodes and anodes of LIBs.23,24

In this work, we introduce hafnium oxides (HfO2) as a-SEIs to stabilize Si electrodes. HfO2 has been widely used as high-k dielectrics in the semiconductor industry. Moreover, HfO2 is known for its stability under various conditions,25,26 which may be desirable for LIB applications. We use X-ray photoelectron spectroscopy (XPS) to demonstrate the stability of HfO2 coatings by comparing the cycle-aged electrode coatings with freshly prepared coated electrodes. The results show that, unlike other coatings that change their chemical compositions after cycling, HfO2 coatings maintain chemically stability, hence improving the cycling stability of the Si electrode significantly.

Silicon thin film electrodes were deposited on a copper current collector by radio frequency (RF) magnetron sputtering. The sputtering rate was 0.1 nm/s, and the thickness was controlled to be 100 nm.

ALD has been used to grow metal oxide thin films with uniform chemical composition and precisely controlled thickness because of ALD’s self-limiting growth mechanism. Thin films with consistent quality can be grown by ALD conformally on a variety of substrates, including substrates with high aspect-ratios, rough and porous, which tremendously broadens the application field of ALD.27,28 In this work, HfO2 was deposited on Si electrodes and wafers using ALD (Cambridge NanoTech, Inc.) at 300 °C. The Hf atoms were provided by the amide precursor tetrakis(dime-thylamido)hafnium (TDMAH), and the oxidant was H2O. TDMAH and H2O were supplied sequentially into the ALD chamber with TDMAH supplied first. TDMAH was heated up to 75 °C to provide a high enough vapor pressure. The nitrogen carrier gas was provided at a flow rate of 20 sccm (standard cubic centimeters per minute). The pulse time of 20 s was long enough to meet the saturation requirement of each ALD cycle. After deposition of HfO2, a multi-angle Spectroscopic Ellipsometer (J. A. Woollam M3000 V) was used to measure the coating thickness and optical constants (refractive index, n, and extinction coefficient, k) of the thin HfO2 films.
Si and HfO$_2$ coated Si electrodes were used as working electrodes. Lithium metal foil was used as counter and reference electrodes. CR 2025 coin cells (Hohsen) were assembled in an Ar filled glovebox (MBraun) with control of oxygen and moisture concentration below 0.1 ppm. A microporous membrane (Celgard 3501) was used as the separator. 1 M LiPF$_6$ in ethylene carbonate and diethyl carbonate (EC:DEC 1:1 volume ratio, BASF) was used as the electrolyte. The Biologic VMP3 was used to cycle the coin cells between 1.2 and 0.05 V vs. Li/Li$^+$ under a charge/discharge rate of C/3 (1 C corresponds to 3600 mA/g). Electrochemical impedance spectroscopy (EIS) was conducted in two-electrode coin cells at assigned voltages. The coin cells were rest for 24 h until stabilized before EIS measurements. The frequency range applied was 1 MHz to 10 MHz. The fitting of equivalent circuit was performed using the EC-Lab software (Biologic).

A Thermo Scientific K-Alpha XPS system with a monochromatic Al K$_z$ source (1486.6 eV) was used for chemical analysis of coatings and SEIs on the electrodes before and after electrochemical cycling. The post-cycled electrodes were harvested from the disassembled coin cells, washed with dimethyl carbonate (DMC) in the Ar-filled glovebox before transferring to the XPS analysis chamber. The transferring process was completed by a specially designed air-tight transfer holder to avoid sample exposure to air.

During the deposition, a Si wafer was placed adjacent to the Si electrodes in the ALD reaction chamber as a thickness reference. The as prepared HfO$_2$ film on the Si wafer was characterized by ellipsometry to confirm the thickness. The measured thickness for 5 layers, 10 layers, and 20 layers of HfO$_2$ is 0.63 nm, 1.25 nm, and 2.51 nm, respectively. The measurement error is within 3% of the measured thickness.

Fig. 1 is the plot of HfO$_2$ thickness versus ALD layer numbers; the linear growth is an outstanding feature of ALD because HfO$_2$ was deposited atomic layer by atomic layer. The deposition rate (1.25 Å/layer) was calculated by the slope of the growth line, and it matches well with previous studies of HfO$_2$ growth.$^{26,27,29,30}$

Fig. 2 shows the cycling performance of bare Si electrodes, Si coated with 5 layers (0.63 nm), 10 layers (1.25 nm), and 20 layers (25.1 nm) of HfO$_2$ under the constant current with a charge/discharge rate equivalent to C/3 (C = 3600 mA/g). Fig. 2 (left) shows capacity retention. The first cycle discharge capacity is about 3600 mA h/g and then stabilized around 2800 mA h/g for all samples. After 100 cycles, the Si electrode coated with 20 layers of HfO$_2$ shows 2019.58 mA h/g capacity, with 70.1% capacity retention. In comparison, the bare Si electrode without coating only shows a capacity of 1331.73 mA h/g after 100 cycles, with 45.9% capacity retention. The Si electrodes coated with 5 and 10 layers of HfO$_2$ show improved performance, but not as good as that of 20 layers. The Coulombic efficiency (CE) is an important indicator to evaluate the performance of LIB electrodes. Fig. 2 (Right) shows the CE of different samples. The first cycle CE was 68.3%, 79.7%, 78.6%, and 78.5% for the bare Si electrode, with 5, 10, and 20 layers of HfO$_2$ coatings, respectively. The low first cycle CE can be attributed to the formation of the SEI on the electrodes and stainless steel conducting coin-cell cases. The results show that, with the HfO$_2$ coatings, the first cycle CE has been improved, due to the suppressed formation of the SEI on the electrodes. The CE for coated samples raised above 99% during the first 20 cycles, in comparison with bare Si samples, which is lower than 99%. The majority of the reactions during SEI formation is caused by electrolyte reduction. The improved CE for coated samples indicates that, compared with naturally formed SEIs, HfO$_2$ coatings can be a more effective in blocking the electrons from contributing to electrolyte reduction reactions.

To characterize the kinetic properties of the coated Si electrodes, EIS was carried out before and after cycling. Fig. 3 shows the Nyquist plots of AC impedance spectra recorded for bare Si electrodes and Si coated with HfO$_2$.
coatings at open circuit potential before and after cycling. The semi-circle (in the high frequency region) originates from the interfacial resistance ($R_{\text{int}}$). The low frequency tail of EIS spectra corresponds to the semi-infinite diffusion or Warburg resistance. By fitting the semi-circles, we obtained the interfacial resistance which is given in Table I. For the fresh electrodes before cycling, the HfO$_2$ coatings can significantly reduce the $R_{\text{int}}$ from 600 $\Omega$ (bare) to 200–300 $\Omega$ (coated). We also compared the $R_{\text{int}}$ after 10 cycles, when the surface passivation has been stabilized. After 10 cycles, Si electrodes coated with 20 layers of HfO$_2$ have the lowest $R_{\text{int}}$ (71 $\Omega$), and compared with bare Si w/o coating, all HfO$_2$ coated samples show reduced $R_{\text{int}}$ (100 $\Omega$ for 5 layers of HfO$_2$, 79 $\Omega$ for 10 layers of HfO$_2$, and 117 $\Omega$ for bare Si electrodes). The increased resistance results in incomplete charge/discharge of the cells, especially with increasing the cycling rate. The reduced $R_{\text{int}}$ for 20 layers of HfO$_2$ coated on Si electrodes indicates that the HfO$_2$ coating reduces the $R_{\text{int}}$ to more favorable values.

Fig. 4 compares the cyclic voltammetry (CV) curves of the bare Si electrode and 20 layers of the HfO$_2$ coated Si electrode for the 1st and 2nd electrochemical cycles. There are three reduction peaks for the bare Si electrode in the 1st cycle: the peak around 0.5 V corresponding to the formation of the SEI and two peaks around 0.2 V and 0.1 V corresponding to Li insertion into Si electrodes. There are also two oxidation peaks during the reverse scan, corresponding to the Li extraction peaks, which match with the insertion peaks during the reduction scan. However, due to the irreversibility of SEI formation, there is no oxidation peak accounted for SEI formation. For the 2nd cycle, the formation of the SEI is largely complete; therefore, there are only two peaks each for Li insertion/extraction. For the Si electrode coated with HfO$_2$, the SEI formation has been suppressed as seen from the absence of the SEI formation peak around 0.6 V. This result can be correlated with the first cycle CE, which has been discussed earlier in this paper. However, the first cycle reduction curve is not perfectly overlapping with the 2nd cycle, which means that there is still addition SEI formed, but the reactions are likely different from those on the bare Si electrodes.

XPS was used to track the changes of HfO$_2$ coatings before and after cycling. Ar sputtering was used for depth profiling. Figs. 5(a) and 5(c) show the HfO$_2$ coated on the Si electrode before cycling: (a) shows that only Hf$^{4+}$ was found on the top surface of the HfO$_2$ coating; (c) shows that both Hf$^{4+}$ and metallic Hf$^{0}$ were found with longer sputtering time and approached to the HfO$_2$ and Si interface. There are two possible reasons for the existence of Hf$^{0}$: (1) the ion sputtering preferentially removes oxygen; and (2) metallic Hf is segregated to the Si/HfO$_2$ interface. Figs. 5(b) and 5(d) show the Hf 4f XPS spectra of the cycle-aged electrode. For both Figs. 5(b) and 5(d), we observed the similar peaks to those of fresh samples. Unlike other metal oxide ALD coatings, such as Al$_2$O$_3$, TiO$_2$, and SiO$_2$, HfO$_2$ coatings show good stability on the Si electrode upon cycling. Since the formation of LiMOx ($M$ = Al, Ti, Si, etc.) is also a Li consuming process, the stability of HfO$_2$ can help prevent additional Li loss during electrochemical cycling.
Fig. 6 shows the depth profile of atomic percentage for the electrodes after cycling. Both electrodes show the existence of Li, O, P, C, F, and Si elements, and the HfO$_2$ coated sample shows, as expected, Hf signals. The Hf can be detected even after approximate 20 nm of sputtering, due to the surface roughness of Si thin-film electrodes. The low percentage of P-2p means that most of the electrolyte molecules has been cleaned by DMC. The F signal is accounted for by the existence of LiF in the SEI. It is generally believed that LiF is favorable for improving the performance of the Si electrode. The F signal is accounted for by the existence of LiF in the SEI. It is generally believed that LiF is favorable for improving the performance of the Si electrode. There is a higher F concentration for the HfO$_2$ coated Si electrode, although the mechanism is still unclear. The percentage of Si is an indication of the thickness of the SEI: the more Si detected corresponding to less SEI founded at the detected depth level. In our experiment, the detection of Si on the HfO$_2$ coated sample increased more rapidly with the increase in the sputtering time, which indicates that less or thinner SEI was formed on the HfO$_2$ coated Si electrode. Our results indicate that HfO$_2$ is chemically stable during the battery operation. This indication is consistent with the fact that the formation enthalpy should be very high for the formation of a stable Li$_x$HfO$_y$ compound (either high temperature or high pressure is necessary to make this compound). In addition, it also shows that the Li ion is able to transport through the amorphous and nanometer thick thin film. But the kinetics of Li diffusion through amorphous HfO$_2$ needs further theoretical exploration.

In conclusion, HfO$_2$ coatings have been shown to be an effective surface passivation layer on the Si electrode to prevent the chemical degradation. As a highly insulating material, HfO$_2$ can effectively block the electrons that play an important role in reducing the electrolyte. Compared with other oxide coatings, we found HfO$_2$ to have a better stability under electrochemical cycling. In addition to previously recognized desirable properties of artificial SEIs, such as electronic insulating, ionic conducting, and mechanically “tough,” we show in this work that the chemical stability is also desirable to achieve the long cycle life and shelf life. We envision that this work will provide helpful guidelines to design better a-SEI for Li-ion cells.

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