



# Mitigating irreversible capacity losses from carbon agents via surface modification



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## HIGHLIGHTS

- Synthesis of ultrathin, conformal coating with atomic/molecular layer deposition.
- Mitigated parasitic reactions for the electrode additives via surface modification.
- Integrated organic fragments in coating chemistry for flexible, conductive coatings.
- Demonstrated the versatility and compatibility of atomic/molecular layer deposition with lithium-ion battery technology.

## ARTICLE INFO

### Article history:

Received 4 August 2014

Received in revised form

22 October 2014

Accepted 7 November 2014

Available online 8 November 2014

### Keywords:

Lithium-ion battery

Atomic layer deposition

Molecular layer deposition

Irreversible capacity loss

## ABSTRACT

Greatly improved cycling performance has been demonstrated with conformally coated lithium-ion electrodes by atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. This paper reports the impact of coating on the electrode additives towards mitigating undesired parasitic reactions during cycling. The ALD and MLD coatings with conformality and atomic scale thickness control effectively stabilize the surface of the electrode components, and the current collector, resulting in the increase of coulombic efficiency throughout cycling. The organic fragment integrated into the recently developed MLD process allows the coating to possess excellent mechanical properties and enhanced ionic conductivity, which significantly reduces cell polarizations throughout cycling. This work validates the importance of ALD and MLD as surface modifiers and further demonstrates their versatility and compatibility with lithium-ion battery technology.

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## 1. Introduction

The high electrical conductivity and chemical inertness of carbon black (CB) have led to its widespread use as a conducting additive [1–6] for manufacturing positive and negative electrodes in lithium-ion batteries. It is generally accepted that the role of the conducting agent is to pave the electrical pathways to electronically connect the electrochemically active particles throughout the laminated electrodes. Nevertheless, the negative impact of the conducting agent on the electrode performance has been continuously overlooked.

Previous works have shown that the irreversible capacity of both cathodes and anodes strongly depend on the content of CB in the composite electrodes [6–9]. There have even been several reports on CB as a potential anode material for lithium-ion batteries [10–14]. However, it has been found to give a relatively low charge–discharge capacity and a large first-cycle irreversible capacity, due to the intrinsic properties of the CB material. Due to the high surface area compared to the active materials, electrolyte reduction on the CB is likely to contribute substantially to the irreversible capacity through the formation of a solid electrolyte interphase (SEI) layer. Thereby, it is essential to study the effects of all the electrode components individually, and potentially attempt to mitigate the negative outcomes from each component. In this study, we focus on the irreversible capacity losses attributed to CB

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conductive agents and their mitigation via surface coating modifications.

Since irreversible reactions occurring on the electrode surface lead to capacity losses, an intuitive prevention method would be to modify the surface using a passivating layer. As demonstrated in previous work, ALD and MLD have been successfully implemented to passivate the liquid electrolyte/electrode interface from irreversible capacity losses [15–21]. The aforementioned works used ALD [15–20] to coat cathode and anode composite electrodes, and MLD [21] to coat high capacity anode composite electrodes, successfully improving the performance of both. These relatively new strategies have been continuously proven to be highly effective in enhancing the electrochemical performance of lithium-ion electrodes. Inspired by the results from such works, we focused on using ALD and MLD surface modification on electrodes containing only CB and polyvinylidene difluoride (PVDF) binder enabling a true identification and mitigation of the irreversible capacity losses attributed to the CB conductive additives, further corroborating the importance of surface coating via ALD and MLD.

## 2. Experimental

### 2.1. Material preparation

Material preparation of the CB-PVDF based composite electrodes was arranged by spreading CB powder ( $75 \text{ m}^2 \text{ g}^{-1}$  surface area, Alpha Aesar), and PVDF mixed in N-methyl pyrrolidinone solvent (1:1 wt. ratio) on a piece of Cu foil. Once the electrodes were dried and calendared some were treated with ALD and others with MLD coating. Before assembling the cells the  $\frac{1}{2}$ " punched electrodes were dried overnight ( $120^\circ\text{C}$ ) in a vacuum oven. Cells were assembled in an Ar-filled glove box and tested at room temperature. Electrochemical measurements were all normalized based on the mass of CB in each electrode.

### 2.2. Surface coating application

ALD  $\text{Al}_2\text{O}_3$  (AO) films were grown directly on the CB-PVDF composite electrodes using a pancake reactor [19]. The typical growth rate for the AO chemistry in this static reactor is  $\sim 2 \text{ \AA}$  per cycle. AO ALD has a typical growth rate of  $1 \text{ \AA}$  per cycle in traditional viscous flow reactors. It is higher in a static reactor due to imperfect purging and higher surface area materials. The AO reaction sequence was: i) trimethylaluminum (TMA) dose to 1.0 Torr; ii) TMA reaction time; iii) evacuation of reaction products and excess TMA; iv)  $\text{N}_2$  dose to 20.0 Torr; v)  $\text{N}_2$  static time; vi) evacuation of  $\text{N}_2$  and any entrained gases; vii)  $\text{H}_2\text{O}$  dose to 1.0 Torr; viii)  $\text{H}_2\text{O}$  reaction time; ix) evacuation of reaction products and excess  $\text{H}_2\text{O}$ ; x) dose  $\text{N}_2$ ; xi)  $\text{N}_2$  static time; and xii) evacuation of  $\text{N}_2$  and any entrained gases. Steps iv, v, and vi were repeated 5 times between TMA and  $\text{H}_2\text{O}$  doses. This sequence constitutes of one cycle of ALD AO. The electrodes were coated with 20 cycles of AO ALD and the reaction was conducted at  $180^\circ\text{C}$ .

MLD aluminum alkoxide, inorganic–organic films were also grown directly on CB-PVDF composite electrodes using a pancake reactor [19]. The typical growth rate for the particular inorganic–organic chemistry used in this work is of  $7.5 \text{ \AA}$  per cycle. The inorganic–organic reaction sequence was: i) Dose inorganic-metal for 2 s, ii) hold inorganic-metal pressure static for 90 s, iii) flow purge for 180 s, iv) 5 cycles of argon static purge, v) dose organic molecule for 2 s, vi) hold organic pressure static for 120 s, vii) flow purge for 240 s, viii) 7 cycles of argon static purge. Flow purge is performed by pumping out excess precursors and reaction byproducts while flowing argon through the reactor. Argon static purge is performed by dosing argon for 20 s, holding argon pressure

static for 5 s, pumping for 45 s, and flow purging for 20 s. This sequence constitutes of one cycle of MLD inorganic–organic film. The electrodes were coated with 10 cycles of inorganic–organic MLD and the reaction was conducted at  $140^\circ\text{C}$ .

### 2.3. Electrochemical measurements

Electrochemical measurements were carried out using an Arbin™ 2000 battery test station and a Biologic battery test station. All cells were assembled in an Ar-filled glove box using the as-prepared bare, ALD coated, and MLD coated CB-PVDF electrodes as the working electrodes and lithium metal foil as the counter electrode. The electrolyte was 1 M  $\text{LiPF}_6$  dissolved in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), the separator was a glass micro-fiber disk (Whatman™ GF/F) and the shell was a stainless steel CR2032 coin cell (Pred. Materials). We used a constant current constant voltage (CCCV) testing scheme to cycle the cells and used a potential range of 0.05–1.5 V vs.  $\text{Li/Li}^+$ . The cells were discharged (lithiated) and charged (delithiated) with a current of  $50 \mu\text{A mg}^{-1}$  of CB for the first 10 cycles and a current of  $100 \mu\text{A mg}^{-1}$  of CB for subsequent cycling between various voltage ranges including that of an anode and a cathode.

Electrochemical impedance spectroscopy (EIS) was performed using the Biologic VMP3. The AC impedance measurements were recorded using a signal with an amplitude of 5 mV and a frequency from 1 MHz to 10 mHz. EIS were conducted for different electrochemical cycles, especially focused in the fully lithiated state of charge (0.05 V vs.  $\text{Li/Li}^+$ ). To further study the redox reactions occurring at higher potentials than those utilized for the electrochemical measurements (0.05–1.5 V vs.  $\text{Li/Li}^+$ ), cyclic voltammetry was applied to both CB-PVDF electrodes containing a copper (Cu) current collector and aluminum (Al) current collector in representation of an anode and cathode electrode, respectively. Cyclic voltammetry was performed using a potential range of 2–4.5 V for the CB-PVDF electrode using the Cu current collector, and 2–5 V for CB-PVDF electrode using the Al current collector and both of these were conducted at a scan rate of  $10 \text{ mV s}^{-1}$ .

### 2.4. Physical characterization

Material Characterization was done with the use of a focused ion beam, FIB (FEI, NOVA200 dual beam system), equipped with and air-lock chamber to prepare the transmission electron microscopy (TEM) samples.  $\text{Ga}^+$  ion source is used for FIB sectioning. The use of an air-lock system enables the observation of lithiated CB-PVDF electrodes without any exposure to air. Air exposure on lithiated sample causes drastic structural changes due to oxidation. However, this mobile air-lock system maintains a vacuum state while samples are loaded from the glove box to the FIB chamber [22].

TEM analysis was performed with a FEI Tecnai F20 operated at 200 keV. TEM samples are prepared using our FIB air-lock system, described in the previous work [23]. A typical TEM sample preparation sequence follows: (1) Pt deposition for the protection of the desired surface area. (2) Cross-sectioning of the electrode with  $\text{Ga}^+$  source. (3) Cross-sectional sample ( $10 \mu\text{m} \times 5 \mu\text{m} \times 0.1 \mu\text{m}$ ) lift-out and attachment to Cu TEM grid using a manipulating probe (100.7™, Omniprobe). (4) Further sample thinning with a beam condition of 10 kV and 30–50 pA is performed until a 50–90 nm thickness is achieved (optimized conditions for TEM observation).

## 3. Results and discussion

TEM and Fast Fourier Transform (FFT) were utilized to characterize the microstructure of the CB-PVDF electrodes employed in this work. Fig. 1 presents TEM images (Fig. 1a–d) and FFT (inset in

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