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Aluminium Inter-Diffusion into $LiCoO_2$ Using ALD for High Rate Lithium Ion Batteries

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Abstract

Here, as with previous work, atomic layer deposition has been used to deposit Al_2O_3 on positive electrode active materials, $LiCoO_2$, to create a protective barrier layer, supress the high potential phase transition and thus reduce the subsequent Co dissolution. However, in this study it was found that it also resulted in the reduction of the charge transfer resistance at the positive electrode-electrolyte interface, thus enhancing the performance of the battery. Energy-dispersive X-ray spectroscopy, in conjunction with transmission electron microscopy, shows that a discrete Al_2O_3 shell was not formed under the selected growth conditions and that the Al diffused into the bulk $LiCoO_2$. The resulting active oxide material, which was significantly thicker than the nominally ALD growth rate would predict, is proposed to be of the form $LiCoO_2$:Al with amorphous and crystalline regions depending on the Al content. The cells consisting of the modified electrodes were found to have good cycling stability and discharge capacities of ~110 $mAhg^{-1}$ (0.12 mAh/cm^2) and ~35 $mAhg^{-1}$ (0.04 mAh/cm^2) at 50C and 100C respectively.

Introduction

Lithium ion batteries (LIBs) have been used in portable electronics for years due to their high energy density and long lifetime. The demands of electrical vehicles and hybrid vehicles however require batteries with a higher rate capability than currently achievable. Positive electrode active material, $LiCoO_2$ (LCO), has a theoretical charge capacity of 272 $mAhg^{-1}$ but has a cut-off limit of 4.2 V which produces a charge capacity of ≈ 160 $mAhg^{-1}$. When charged above 4.4 V a phase transition occurs due to the deintercalation of greater amounts of Li ions inducing partial oxidation of the Co^{3+} to the unstable Co^{4+} and as a consequence dissolution of Co into the electrolyte. This loss of Co quickly degrades the performance of the battery.[1] The expansion due to the phase change also degrades the commonly used binder, Polyvinylidene fluoride (PVDF)[2] used in the electrode assembly hence stabilising the $LiCoO_2$ is imperative to realise higher capacity LIBs.

The decomposition of the electrolyte on the positive electrode surface leads to the formation of the solid electrolyte interface (SEI) consisting of amorphous Li complexes[3] which severely inhibits the carrier transport. To this end, metal oxide layers have been applied to the $LiCoO_2$ material to supress the phase transition and the dissolution of Co, for example, ZrO_2,[4] TiO_2,[5] HfO_2[6] and Al_2O_3[7]. In addition to an immediate physical barrier the relatively wide band gap of these metal oxides deter diffusion of electrons generated from redox reaction into the liquid electrolyte, thus maintaining stability under extended use.[8] Furthermore, the high fracture toughness of selected oxides further improves the coating effectiveness.[3]

Previous work on Al_2O_3 as a protective coating has investigated both negative [9] and positive electrodes[10] and has shown that the cycle lifetime is significantly improved. However, as Al_2O_3 is an insulator and does not act as an active material, the over loading into the active medium has

also been noted to decrease the electric capacity. Atomic layer deposition (ALD) is a highly conformal and self-limiting deposition method that is well suited to depositing a thin protective layer. The highly conformal and pin hole free coverage that can be obtained with ALD allows the protective coating to be thinned even to the sub nanometre scale, resulting in little sacrifice in the capacity, and maintain its efficacy. As the native SEI on LCO has been shown to be 2 – 5 nm thick,[11] the application of ALD to generate ultrathin layers has significant implications for improving the Li ion transport during charge and discharge. Previous reports of Al_2O_3 coated LCO material have generally applied discreet coatings of Al_2O_3 to the positive electrode powders before the preparation of positive electrode sheet including active materials, binder and current collector.[12] However, application of protective coatings to an assembled positive electrode sheets has the potential to be more effective as it will minimise the internal resistance between particles in the bulk electrode.[13, 14] It should be noted that when the protective coating is applied to the assembled positive electrode, the nature of the binder material must be considered, for example, the commonly used PVDF has thermal restrictions that prevent ALD process temperatures above 150°C.

ALD of a passive protective coating of Al_2O_3 on powders or films has been shown to be effective in increasing cycle lifetime and stability at high voltages. In all the ALD studies it was observed, or presumed, that the Al_2O_3 was a discrete layer.[12, 13, 15 -17] In comparison non-ALD methods have, in addition to creating distinct layers, intentionally doped the electrodes of lithium ion based battery systems with Al. The reduction of electrode resistance following the inclusion of Al is observed in $LiCoO_2$,[18] $Li_4Ti_5O_{12}$,[19, 20] $Li_2Na_2Ti_6O_{14}$,[21, 22] $LiNiO_2$,[23] $Li_3V_2(PO_4)_3$,[24] $LiNiO_2$,[25] $LiCrTiO_4$[26] and $LiMn_2O_4$.[27-30] Theoretical[31] and subsequent experimental studies have shown the improved performance of $Li(Al, Co)O_2$ over LCO positive electrode materials.[7, 18, 32-

[36] The incorporation of Al into the LCO material produces structural and chemical changes. Increased Al content results in an expansion along the *c*-axis. This reduces lattice movement at high voltage and so limits the breakdown of the LCO material. Direct comparison of Al doped and Al_2O_3 coated LCO was made by Woo et al. who found that the directly doped material was more stable under higher rates.[16] In this study we demonstrate that the Al_2O_3 ALD process can, under the correct conditions, dope the LCO material without the need for a post deposition annealing step. This process gives a material that maintains cell capacity even during extremely high charge and discharge rates.

Experimental

Modified positive electrodes were fabricated employing LCO powder with an average grain size of ca.3μm (Cell Seed, Nippon Chemical) as the active material. A 7:2:1 weight ratio of the LCO powder, acetylene black and PVDF was thoroughly mixed together with the solvent, N-methyl-2-pyrrolidone (NMP), to produce a paste. This paste was then spread on an Al foil current collector and dried.[37, 38] The resulting electrode thickness was 8.2 μm and the loaded mass of the active material for one coin cell was 3.3 mg. Nominal Al_2O_3 thicknesses of 1, 2, 3 and 4 nm were deposited by ALD on the LCO positive electrode material; it should be noted that the electrodes were stored in air for a month prior to ALD. The ALD process was performed at 150°C in a Picosun R200, pulse times for reagents were 0.1 second for both trimethylaluminium (TMA) and water with purge times of 4 and 6 second respectively. The growth rate was presumed to be 0.1 nm per cycle.[39] Type 2032 coin cells were assembled under argon with a solution of 1 mol dm^{-3} $LiPF_6$ in EC:DEC (3:7 v/v) as the electrolyte and Li metal acting as the counter electrolyte. The cells were first charged and discharged at 0.1C (1C = 160 mA/g) for five cycles and then the charge–discharge rate was increased stepwise, to an ultrahigh rate of 100C, for five cycles at

each rate. After a total of 50 cycles the charge-discharge rate was returned to 0.1C. The impedances of the cells during charging and discharging were measured with an alternating current (AC) amplitude of 10 mV for frequencies from 5 mHz to 1 MHz, during which the cells were charged and discharged under constant current–constant voltage (CC-CV) with a voltage window of 3.3–4.5 V at 10C. [40]

Results

As shown in figure 1, when compared to the bare LCO, all Al_2O_3 coated samples displayed superior discharge capacity performance at all rates, with the improvement being more obvious at the higher rates. Of the coated samples, the nominally 3 nm thick ALD sample's performance was the greatest improvement, retaining a charge capacity of ~35 $mAhg^{-1}$ (0.04 mAh/cm^2) even at an ultrahigh rate, 100C. Figure 2 illustrates the relative performance of LCO cells at the high charging rates of 20 and 50C for the differing coating thicknesses, from which it can be seen that the nominally 3 nm Al_2O_3 coated sample with a capacity of ~110 $mAhg^{-1}$ (0.12 mAh/cm^2) at 50C displayed the best performance.

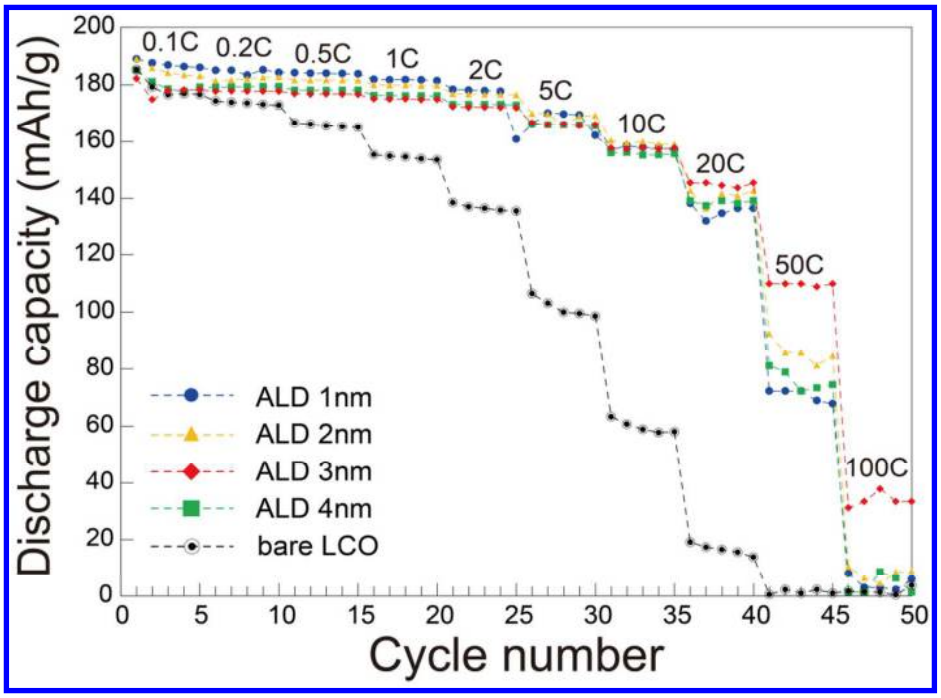

Figure 1. Comparison of the discharge capacity performance of bare LCO and all Al_2O_3 coated LCO samples.

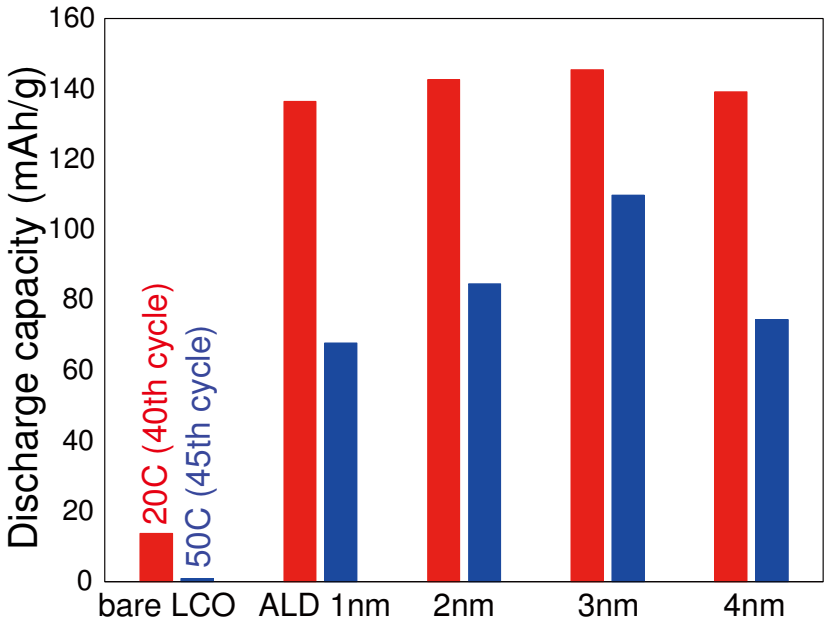

Figure 2. Relative performance of LCO cells at the high charging rates of 20 and 50C for differing Al_2O_3 coating thicknesses.

The observation of high performance characteristics of the cells with the relatively thick 3 nm ALD Al_2O_3 coating is at odds with previous studies.[10] To elucidate reasons for this anomaly the 3 nm Al_2O_3 coated sample was chosen for further analysis.

An SEM image of the LCO material coated with a nominal 3 nm layer of Al_2O_3, displaying maximum high rate capabilities, is given in figure 3. The terrace morphology of the bare LCO attributing to the basal plane of layered rock salt structure can still be seen in the coated sample, however, evidence of surface blisters imply that the sample has undergone surface modification during the ALD process or that the ALD growth is atypical for Al_2O_3.

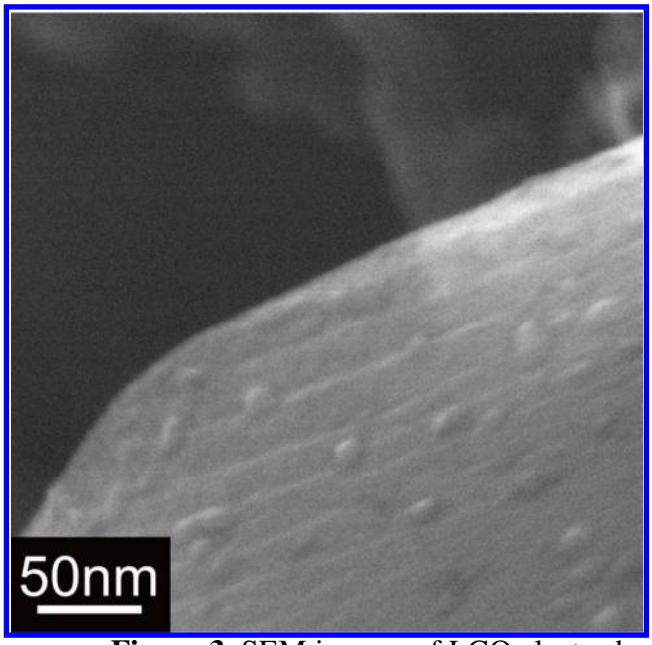

Figure 3. SEM images of LCO electrode coated in a nominal 3 nm layer of Al_2O_3

The crystalline and amorphous nature of the LCO and Al_2O_3 respectively can be seen in the TEM images of figure 4 from which it is immediately apparent that the thickness of the amorphous Al_2O_3 (~10 nm) is far greater than the nominal growth rate per cycle would predict. The image also lacks a sharp interface between the ALD coating and the LCO material. The

elevated growth rate could be due to incomplete purging of the precursors between ALD half cycles resulting in a significant chemical vapour deposition component in the ALD process.[41] However, the very large discrepancy in growth per cycle indicates it is more likely that the LCO itself has an excess of chemically active sites that can react with trimethylaluminium within the positive electrode. These reactive sites can arise from oxygen defects within the lattice, moisture generating LiOH and Li_2O in the LCO interfacial region[42, 43] or physisorption. These defects within the LCO are not reversible under the ALD reactor conditions employed in this study.

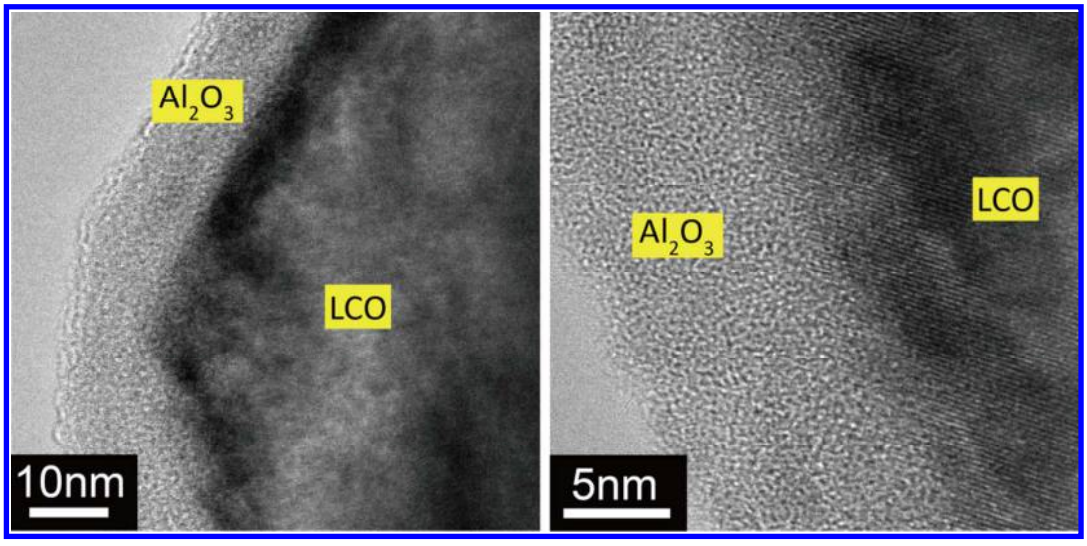

Figure 4. TEM images of the Al_2O_3 coated LCO. A thicker than expected outer layer is observed when a nominal 3 nm of Al_2O_3 is deposited

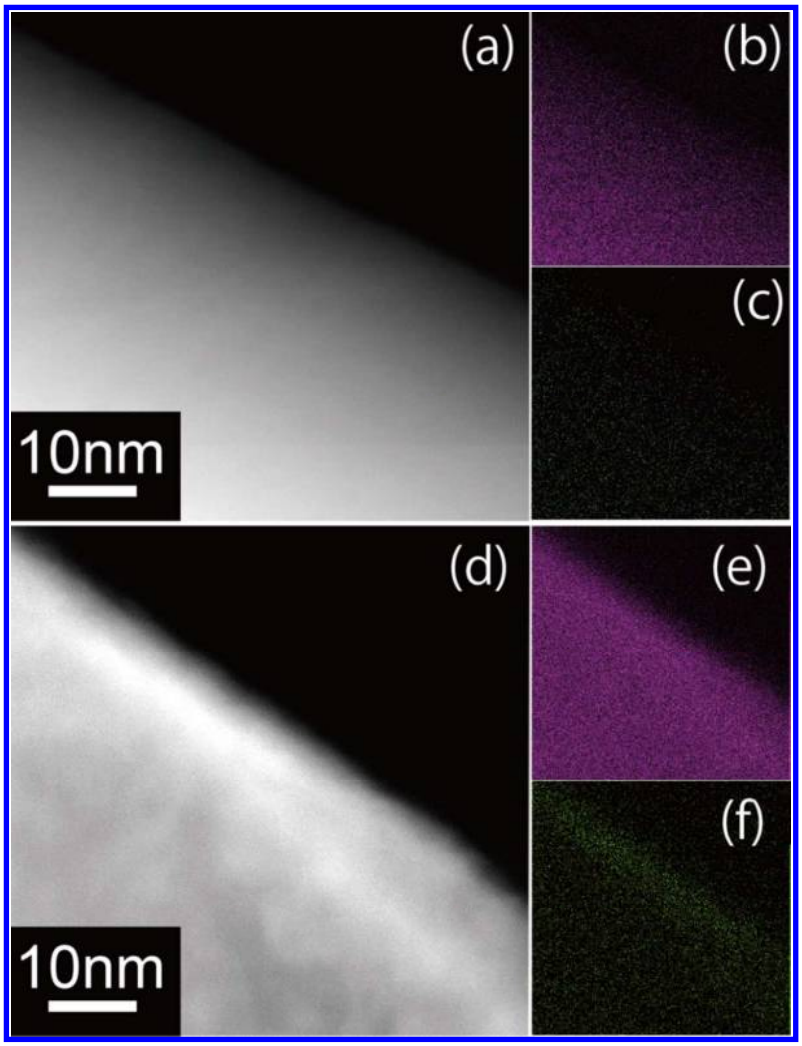

Figure 5. TEM image of bare $LiCoO_2$ (a), EDX images of Co-K (b) and Al-K (c). Figs (d)-(f) indicate those of Al_2O_3 modified LCO.

Elemental analysis of the LCO and its interfacial layer were determined by energy-dispersive X-ray spectroscopy (EDX) of the TEM cross-sectional lamella and shown in figure 5. Figure 5(a)-(c) show Co is present throughout the structure for the bare LCO, whereas the Al was hardly detected. As for the decorated specimens, Al is clearly concentrated at the surface but it has also diffused into the LCO material [Figure 5 (d)-(f)]. These measurements confirm that the Al_2O_3 layer does not form a discrete layer on the LCO surface. Further evidence for the absence of a discrete Al_2O_3 layer was obtained from in-situ electrochemical impedance measurements. The

measured impedance was fitted using the calculated impedances from an equivalent circuit (Supporting Information Figure S1)and associated Nyquist plots (Figure S2) using a non–linear least squares fitting routine. The impedance data, Figure 6 , indicate that the Li electrode resistance (R_{Li}) and that of the electrolyte (R_{sol}) are reasonably constant with the positive electrode charge transfer resistance (R_{ct}) being significantly reduced for the ALD coated sample, an observation that would not be observed if a significant thickness of a highly resistive oxide such as Al_2O_3 was present.

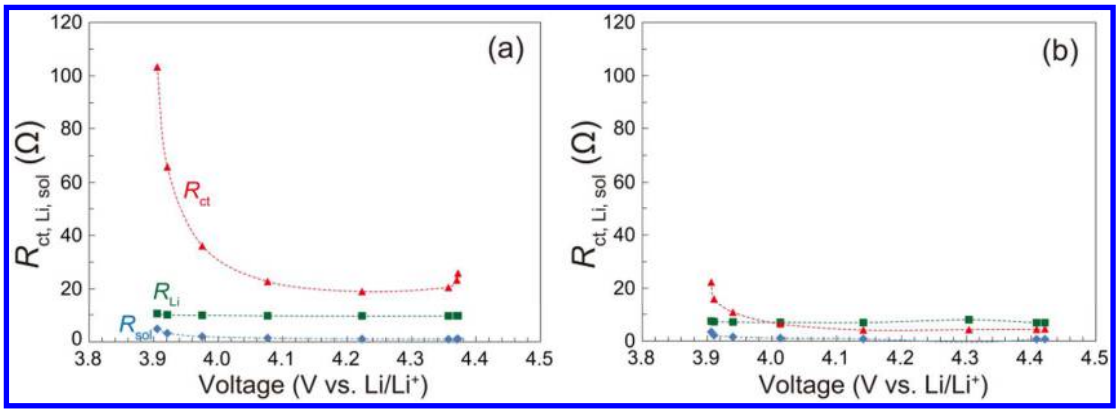

Figure 6. Impedance measurements of (a) bare LCO and (b) Al_2O_3 LCO at 10C charge.

Discussion

In the absence of further data we propose the formation of a $Li(Al,Co)O_2$ layer via the infiltration of Al through an ALD growth process. The mixed metal oxide proposed to be formed here has previously been observed after high temperature anneals of wet chemically grown[44] and radio frequency magnetron sputtered[45] Al_2O_3 layers on LCO. In these previous studies the high thermal budget of an annealing process is necessary to overcome the activation energy for diffusion of the Al_2O_3. However, in this study it is believed that moisture exposure of LCO in air, during electrode storage, generates reactive sites that, although more frequent at the surface, penetrated into the outermost few nanometres of the LCO particles. This combined with the high

reactivity, self- limiting chemistry and ability of TMA to also penetrate such structures could explain the graded incorporation of Al into the structure. Improvement in the performance of the positive electrode material can hence be attributed to the formation of a diffuse outer LCO layer where partial Al substitution of Co is observed. This outer layer possessing improved electrical characteristics in addition to enhancing the structural stability of the active material under charging-discharging cycling.[18, 46, 47] Additionally, it is envisaged that the performance is also enhanced by the action of coating the assembled electrode sheets, rather than individually coated particles, further minimizing the internal resistance of the electrode.

Conclusions

In this study we have shown that ALD coating LCO using trimethylaluminium and water does not always form a discrete Al_2O_3 layer. In this work it is believed that unintentional exposure of the electrodes to moisture in air allowed the penetration of the aluminium precursor to generate an interfacial $LiCo_xO_2$:Al with an outer amorphous shell that was three times greater than the expected thickness and yet still exhibited reduced charge transfer resistance as compared to the bare LCO. The notable reduction in R_{ct} is due to for the partial Co substitution by Al on the nano-scale surface of LCO, leading to suppression of Co dissolution into the electrolyte. The resultant LIB assemblies demonstrated excellent behaviour characteristics, in terms of charging capacity and rates, generating ~110 $mAhg^{-1}$ at 50C and ~35 $mAhg^{-1}$ at 100C, reverting to ~185 $mAhg^{-1}$ at 0.1C after 50 cycles. Future work will investigate the deliberate dosing of water to tune the $LiCoO_2$:Al composition and optimise the resulting battery performance.

Supporting Information

Details of the equivalent circuit model for the impedance of the half-cells and the corresponding Nyquist plots and fits for the measured samples.

Acknowledgements

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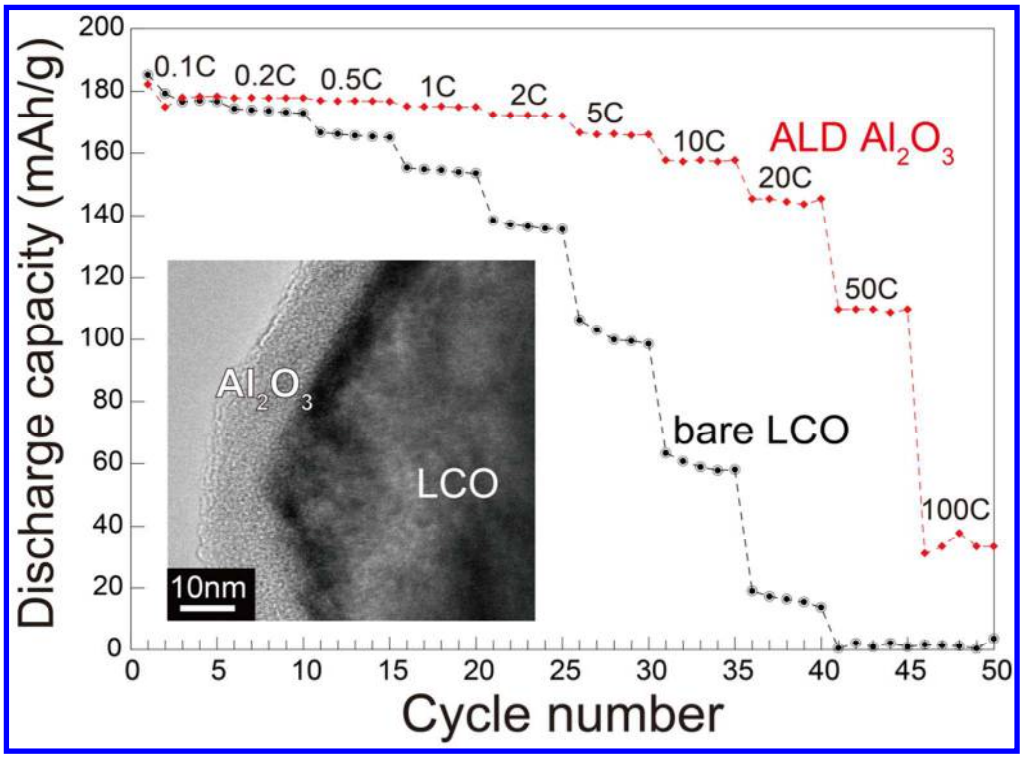
Discharge capacity (mAh/g)
Cycle number
0.1C
0.2C
0.5C
1C
2C
5C
10C
20C
50C
100C
ALD Al2O3
bare LCO
Al2O3
LCO
10nm