

Nanoscale-engineered LiCoO_2 as a high energy cathode for wide temperature lithium-ion battery applications—role of coating chemistry and thickness

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Received 16 December 2021, revised 7 March 2022

Accepted for publication 28 March 2022

Published 20 April 2022



Abstract

Extending the charge cutoff voltage of LiCoO_2 (LCO) beyond 4.2 V is considered as a key parameter to obtain higher energy densities. Following gaps have been identified based on a thorough literature survey especially for higher cutoff voltage of nanoscale engineered LCO cathodes, (i) different metal oxides and metal fluoride surface coatings have been mostly done independently by different groups, (ii) room temperature performance was the focus with limited investigations at high temperature, (iii) nonexistence of low temperature cycling studies and (iv) no reports on high rate capability of LCO beyond 4.5 V (especially at 4.8 V) needs to be investigated. Herein, we report the effect of nanoscale engineering of LCO along with the role of coating chemistry and thickness to study its electrochemical performance at higher voltages and at wide operating temperatures. Surface coating was implemented with different metal oxides and a metal fluoride with tunable thickness. At 4.5 V, 5 wt% Al_2O_3 coated LiCoO_2 ($\text{LCO@Al}_2\text{O}_3$ -5) delivered a reversible capacity of 169 mAh g^{-1} at 100 mA g^{-1} and 151 mAh g^{-1} at high rate of 10 C (2 A g^{-1}) and 72% retention at the end of 500 cycles. At 55°C , it exhibited better stability over 500 cycles at 5 C and even at -12.5°C it maintained 72% of its initial capacity after 100 cycles at 200 mA g^{-1} . At 4.8 V cut-off, $\text{LCO@Al}_2\text{O}_3$ -5 rendered reversible capacity of 213 mAh g^{-1} at 100 mA g^{-1} , a high value compared to literatures reported for LCO. Also noted that it delivered a capacity of 126 mAh g^{-1} at a current density of 1 A g^{-1} , whereas bare could only exhibit 66 mAh g^{-1} under same testing conditions. Enhanced performance of $\text{LCO@Al}_2\text{O}_3$ -5 can be ascribed to the lower charge transfer resistance derived from the stable solid solution formation on the interface. *Ex situ* XRD and *ex situ* Raman analysis at different stages of charge/discharge cycles correlates the enhanced performance of $\text{LCO@Al}_2\text{O}_3$ -5 with its structural stability and minimal structural degradation.

Supplementary material for this article is available [online](#)

Keywords: nanoscale engineering, high voltage LiCoO_2 , structural stability, coatings

(Some figures may appear in colour only in the online journal)

1. Introduction

The wide spread civilization of the modern society escalates the demand for renewable energy sources that compels the

development of a durable and benign electrochemical energy storage technology. Lithium-ion batteries (LIB) gained a prominent position in the commercial market for energy storage since 1990 owed to its high energy and power density,

long life. It is widely used in medical implants, defense, space applications, portable electronics and now have been extended to even large-scale energy storage applications [1–3]. Lithium cobalt oxide (LiCoO_2 , LCO) is the dominated cathode material for LIB applications due to its high operational voltage of 3.9 V, high energy density, scalable synthesis etc. Even though it has a theoretical capacity of 274 mAh g^{-1} , practical capacity is limited to 140 mAh g^{-1} with a charge limit of 4.2 V [4]. Upon extending the charge cutoff voltage beyond 4.2 V, material undergoes structural instability with surface and bulk phase transformations that triggers severe voltage drop, capacity fade and increased cell impedance over cycles. Increased heating effect and oxygen release from the structure heats up the flammable electrolyte that could end up in battery explosions [5–7]. Extending the charge cutoff voltage limit of LCO with minimal structural degradation is of significant interest. The scope is to uplift the flagship cathode LCO for the future high energy density applications. Moreover, the fundamental understanding developed with LCO could be useful for improving the performance of other layered cathode materials.

In a battery configuration, cathode materials with high capacity and operational voltage plays a vital role in the enhancement of energy density [8]. Many strategies such as surface coating, elemental doping, electrolyte modification and morphology control were implemented by researchers to enhance the working voltage and energy density of cathodes [9–14]. Among these strategies, surface coating gained much attention because the coating minimizes the direct electrode-electrolyte contact. This in turn protects the material from irreversible structural transformations propagating from surface to bulk and unwanted side-reactions [15–17]. Numerous researchers across the globe have focused on surface coating of LiCoO_2 by various metal oxides, metal fluorides, metal phosphates, polymers and ionic conductors via different methodologies such as wet-chemical, pulsed laser deposition, atomic layer deposition and heat treatment techniques. It is evident from the literatures that surface modification of LiCoO_2 could be an effective strategy for the improvement of capacity as well as cycling stability at higher charge voltages beyond 4.2 V [18–20]. In spite of significant number of literature on metal oxide and metal fluoride coatings several research aspects are yet to be explored especially for high voltage charge cutoff of LCO ($\geq 4.5 \text{ V}$). Specific aspects include, comparison of different coating chemistries on LCO across literature is not quite straight forward due to variations in parent material preparation method, coating method, coating thickness, differences in particle size, differences in rates tested etc. Also from the performance point of view, lack of high temperature data at high rates and lack of low temperature cycling data for metal oxide/metal fluoride coated LCO is important to be investigated [21, 22].

To investigate the above described gaps, we have implemented engineering of LCO via three different coating chemistries such as TiO_2 , Al_2O_3 and AlF_3 with different coating thickness by simple and facile wet-chemical process. Bare and engineered LCO samples were subjected to electrochemical studies at higher charge cutoff voltages between 4.5 and 4.8 V.

Among all the samples, $\text{LCO@Al}_2\text{O}_3$ -5 exhibited better first cycle discharge capacity of 169 mAh g^{-1} and 213 mAh g^{-1} at higher voltages of 4.5 V and 4.8 V respectively at 100 mA g^{-1} . It offered a good cycling stability and capacity compared with other samples at higher voltages, low temperature (LT), room temperature (RT) and high temperature (HT). To the best of our knowledge, there is no other reports on engineered LCO, especially metal oxide coatings showing 500 cycles stability at higher current rates of 5 C (1 A g^{-1}) and 10 C (2 A g^{-1}) at 4.5 V with enhanced capacity. Even at 55°C , $\text{LCO@Al}_2\text{O}_3$ -5 offered 67% retention over 500 cycles at 5 C. Interestingly, it rendered a stable performance at -12.5°C and 200 mA g^{-1} over 100 cycles. Also, it is noted that there are very limited reports on LCO performance at high current rate of 5 C and high voltage of 4.8 V and our work stands top based on electrochemical performance achieved. $\text{LCO@Al}_2\text{O}_3$ -5 outperformed with better capacity and cycle life at even higher current rates and higher voltages ($\geq 4.5 \text{ V}$) in wide temperature range compared to other samples. It can be assigned to the better Li-ion diffusion kinetics contributed from a co-effect of Al_2O_3 coating and solid solution phase formation on LCO surface that preserves the material structural stability at high voltages.

2. Materials and methods

2.1. Synthesis of LiCoO_2

LiCoO_2 was synthesized via sol-gel process and 25 gm was prepared in order to conduct various studies. Lithium acetate and cobalt acetate salts were taken as the precursors. Stoichiometric amount of precursors were dissolved separately in 10 ml of deionized water and acrylic acid was added to it as a chelating agent under stirring at 70°C . Certain amount of ammonia solution was added to the above solution for neutralization. The obtained gel was dried in vacuum oven at $100^\circ\text{C}/12 \text{ h}$. The resultant was pre-calcined at $450^\circ\text{C}/1 \text{ h}$ followed by a final calcination at $650^\circ\text{C}/10 \text{ h}$ under a ramp of 5°C min^{-1} .

2.2. Engineering of LiCoO_2

As-prepared LCO powder was used for engineering with TiO_2 , Al_2O_3 and AlF_3 coating. LCO@TiO_2 synthesis route was reported by our group in a previous work [23]. Al_2O_3 coating was done by a wet chemical method similar to literature [15]. Stoichiometric amount of $\text{AlN}_3\text{O}_9.9\text{H}_2\text{O}$ was dissolved in DI water. LCO powder was dispersed in it under ultra-sonication for around 30 min and kept under stirring at RT for 12 h. Two sets of samples based on weight ratio of Al_2O_3 with respect to parent material utilized during the coating process, as 2 wt% and 5 wt% were finalized after the optimization at different weight ratios, named as $\text{LCO@Al}_2\text{O}_3$ -2 and $\text{LCO@Al}_2\text{O}_3$ -5 respectively. Centrifugation and washing was done for several times in order to remove the residuals. The resultant was dried at 80°C and calcinated at $500^\circ\text{C}/5 \text{ h}$. LCO@AlF_3 coating was done by following a simple wet chemical method similar to literature [24]. Respective amount of $\text{AlN}_3\text{O}_9.9\text{H}_2\text{O}$ was

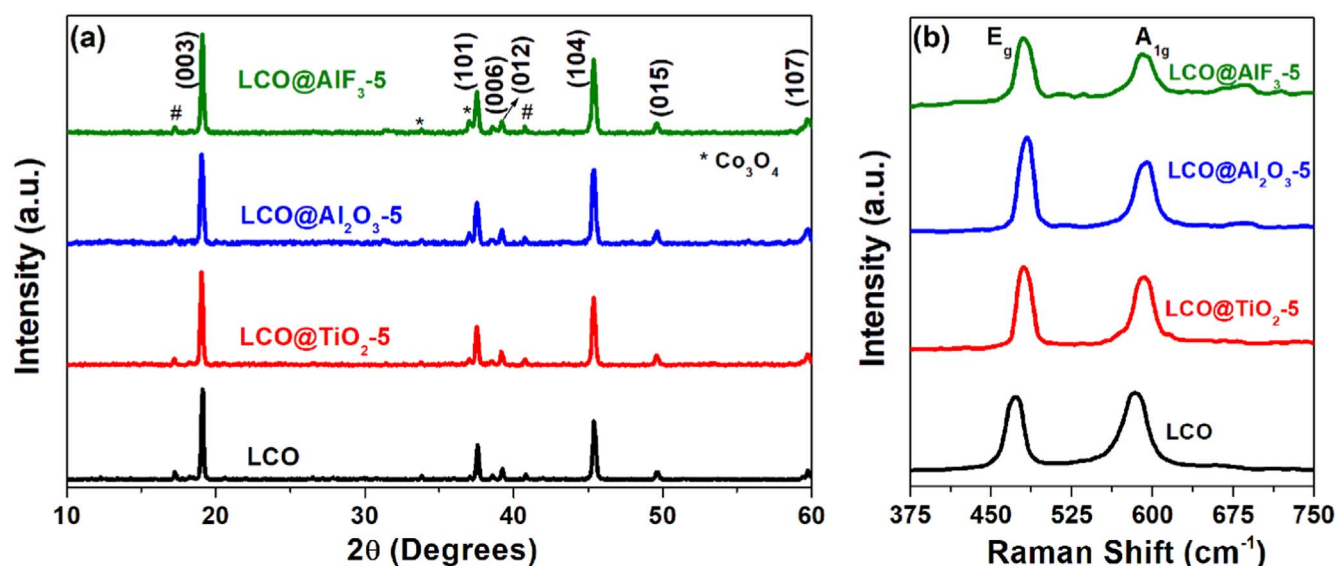


Figure 1. (a) XRD pattern and (b) Raman spectra of pristine electrodes of LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 samples.

dissolved in DI water and LCO powder was immersed into the solution. It was kept for stirring at 50 °C. NH₄F solution was prepared and added to the above solution drop wise. Three sets of samples based on weight ratio of AlF₃ with respect to LCO as 1 wt%, 2 wt% and 5 wt% were finalized after the optimization at different weight ratios. Molar ratio of Al: F was maintained as 1:3. This solution was vacuum dried at 60 °C subsequently annealed at 400 °C/4 h under argon flow to obtain LCO@AlF₃-1, LCO@AlF₃-2 and LCO@AlF₃-5 nanoparticles respectively.

2.3. Material characterizations

X-ray diffraction for all the powdered samples and cycled electrodes were conducted using Cu K_α x-rays from (Bruker AXS D8 Advance, Germany). Raman spectra of pristine and cycled electrodes were obtained from different spots of the samples using Witech Alpha 300 R (Germany) with a diode laser of 633 nm under 15 mW power. Surface images of the samples were recorded with the aid of a Field emission scanning electron microscope JSM 7610FPlus (JEOL, Japan). Morphological analysis of the bare and coated samples were carried out with a high resolution transmission electron microscope (JEOL/JEM 2100, Japan) and surface analysis data of the samples were collected using Axis Ultra spectrometer with mono-chromated Al-K_α as x-ray source having 700 × 300 microns spot size (Kratos, UK). C 1 s calibration was done in the obtained XPS spectra. Scanning transmission electron microscopy imaging and energy dispersive x-ray spectroscopy based elemental mapping of surface coated LCO samples were conducted (FEI TECNAI G², Netherlands).

2.4. Electrochemical measurements

Electrodes were fabricated via conventional slurry casting technique in a composition of 80:10:10 of active material: multi-walled carbon nanotubes: polyvinylidene fluoride respectively mixed with NMP as the solvent and casted on Al

foil which got dried at 80 °C/12 h. Obtained electrodes were having an active loading of 3.1–3.4 mg cm⁻². Swagelok cells were fabricated in an argon filled glove-box with O₂ < 2.0 ppm and H₂O levels < 1.0 ppm (UNILab^{pro} sp, MBRAUN, Germany). For all the cells, lithium foil was taken as the counter electrode with glass microfibers as separator and the electrolyte used was 1 M LiPF₆ in EC: DMC solvent (1:1, PuriEL, Canada). Galvanostatic charge–discharge (1 C = 200 mA g⁻¹), rate capability test and cycling performance were conducted at low temperature (LT –12.5 °C), room temperature (RT 25 °C) and high temperature (HT 55 °C) using battery tester (Biologic Instruments, USA) in all the case discharge voltage was limited to 3.0 V while charge cutoff voltage varied between 4.5 and 4.8 V. Electrochemical impedance studies were performed in a range of 10 mHz–10 kHz under 10 mV ac amplitude. After electrochemical cycling, Swagelok cells were taken inside the glove box and respective electrodes were collected and washed with dimethyl carbonate (DMC). The solvent removed electrodes were stored inside glove box for *ex situ* characterizations.

3. Results and discussions

3.1. Structural, morphological and surface analysis

Structural characterization of bare and coated samples is presented in figure 1. XRD pattern seems consistent for all four samples reported for LCO apart from the occurrence of minor Co₃O₄ peak due to large quantity material synthesis [25]. Peak splitting of (006)/(012) along with other indexed peaks clearly indicates the hexagonal layered structure of the synthesized sample [26]. Characteristic peaks were indexed with respective (hkl) values. Absence of TiO₂, Al₂O₃ and AlF₃ peaks in XRD pattern indicates that they may be amorphous. Lattice parameters of the bare and coated samples were calculated and shown in table S1. The values obtained are almost similar to the literatures reported for LCO. There is

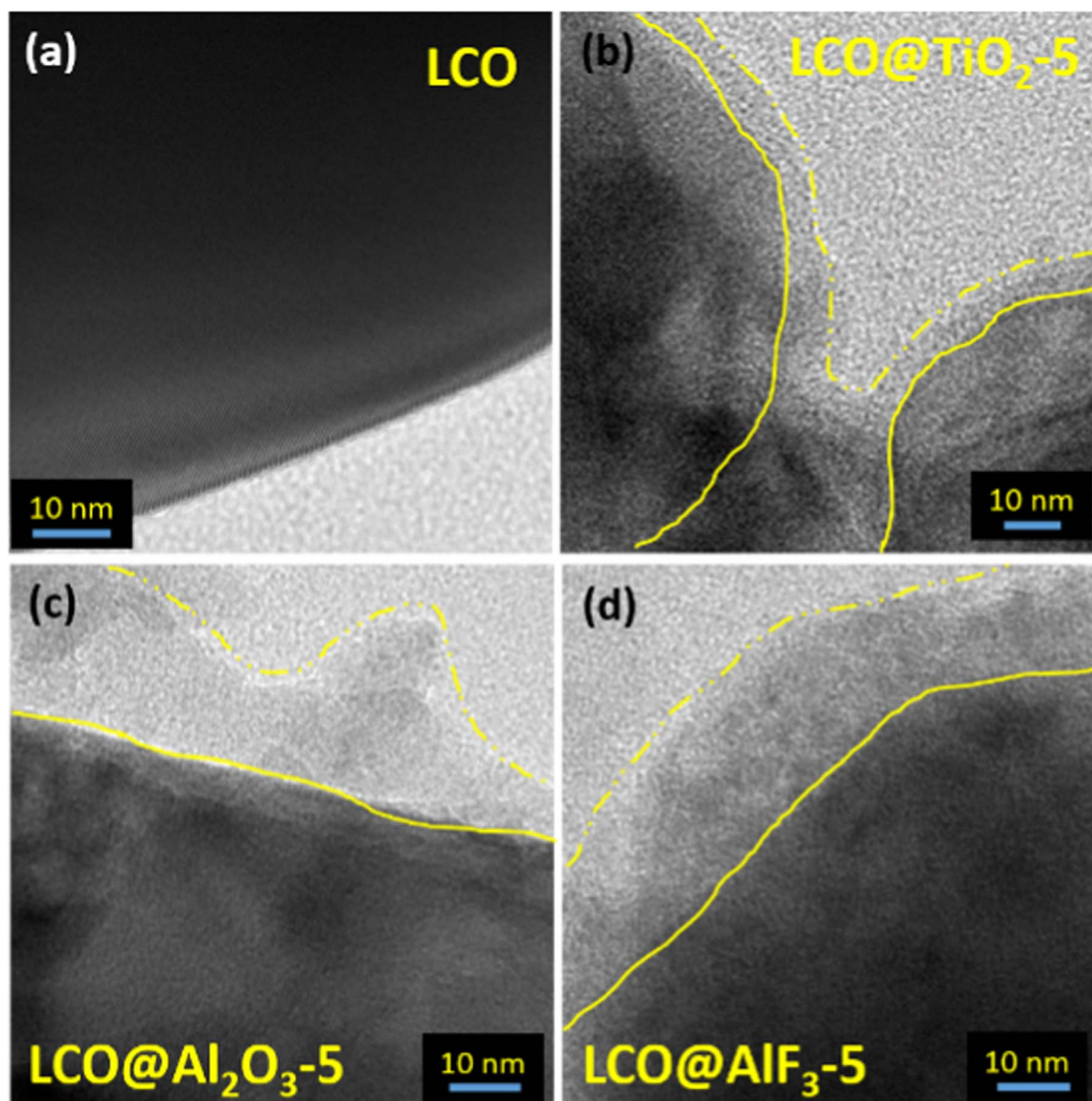


Figure 2. High resolution TEM images of (a) LCO (b) LCO@TiO₂-5 (c) LCO@Al₂O₃-5 and (d) LCO@AlF₃-5.

no significant change in *c*-axis parameter of coated samples compared to bare indicates that coating did not affect the bulk structure. Raman analysis on pristine electrodes of bare and coated samples were conducted and illustrated in figure 1(b). It is seen that for all the samples there exists the two major characteristic Raman peaks of LCO, E_g and A_{1g} which is at almost similar positions reported in previous studies. Due to the less resonance from 633 nm source excitation, E_g appears prominent than A_{1g} [27]. HRTEM images of bare and coated samples are depicted in figure 2. Apart from LCO sample, there exists coating on the surface of other three samples. Coating layer thickness obtained were in a range of 1–2 nm, 10–12 nm and 15–18 nm for TiO₂-5, Al₂O₃-5 and AlF₃-5 coated samples respectively. Also, it is seen that TiO₂ and AlF₃ coatings are uniform, whereas Al₂O₃ coating remains non-uniform over LCO surface. Surface images of bare and coated samples were collected using FESEM and is shown in figure S1 (available online at [stacks.iop.org/NANO/33/](https://stacks.iop.org/NANO/33/275403/mmedia)

[275403/mmedia](https://stacks.iop.org/NANO/33/275403/mmedia)). Bare and coated samples have a particle size of around 150–200 nm. STEM imaging and elemental mapping of LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 samples were conducted to reveal the distribution and semi-quantitative analysis of Co, Al, Ti, F and O elements in the surface coated LCO samples. The obtained metal ratios along with the mapping of LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 samples have been shown in figures S2–S4 respectively. It is observed that for LCO@TiO₂-5, Ti is not uniformly distributed in the mapping area of LCO which could be due to the smaller thickness of the coating, whereas, for LCO@Al₂O₃-5 and LCO@AlF₃-5, Al, O as well as F have been evenly distributed throughout the LCO surface.

Figures 3 and 4 shows the surface chemical analysis of LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 powdered samples. In figure 3(a), peaks obtained at 284.6 eV and 288.3 eV in all four samples correlates to C–C and C–O

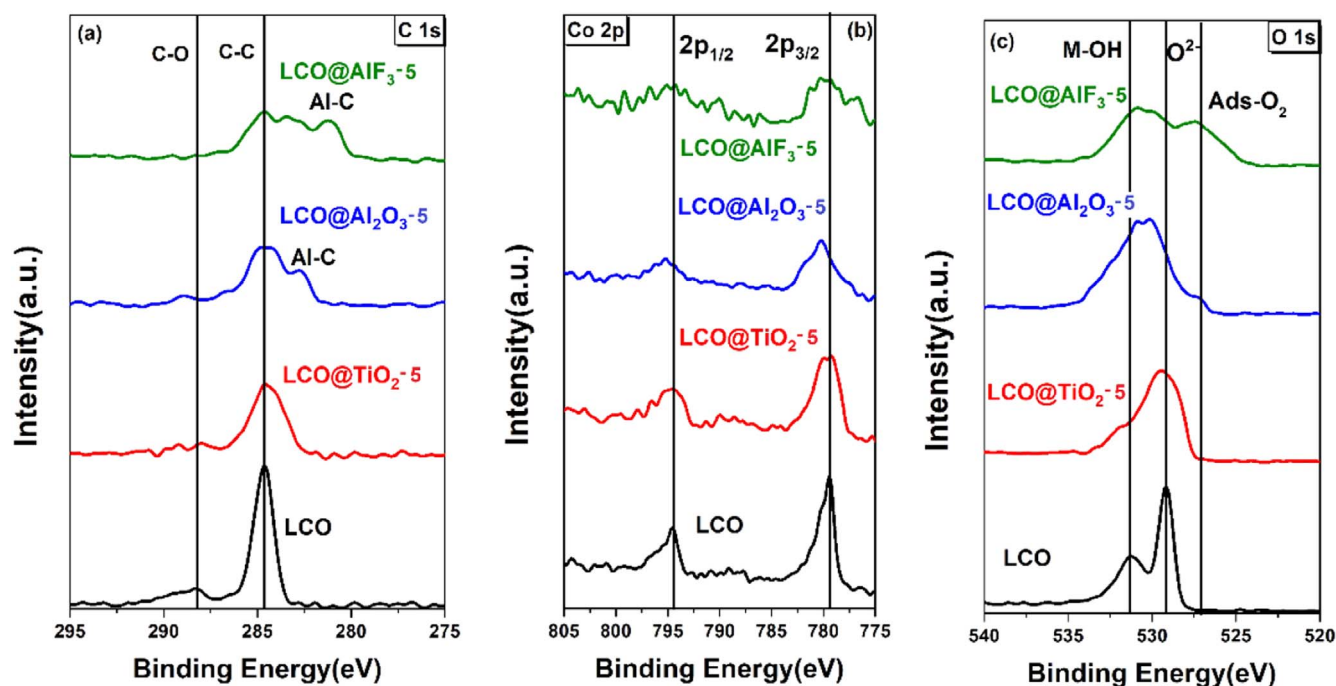


Figure 3. High resolution XPS spectra of (a) C 1 s, (b) Co 2p and (c) O 1 s of bare and coated samples.

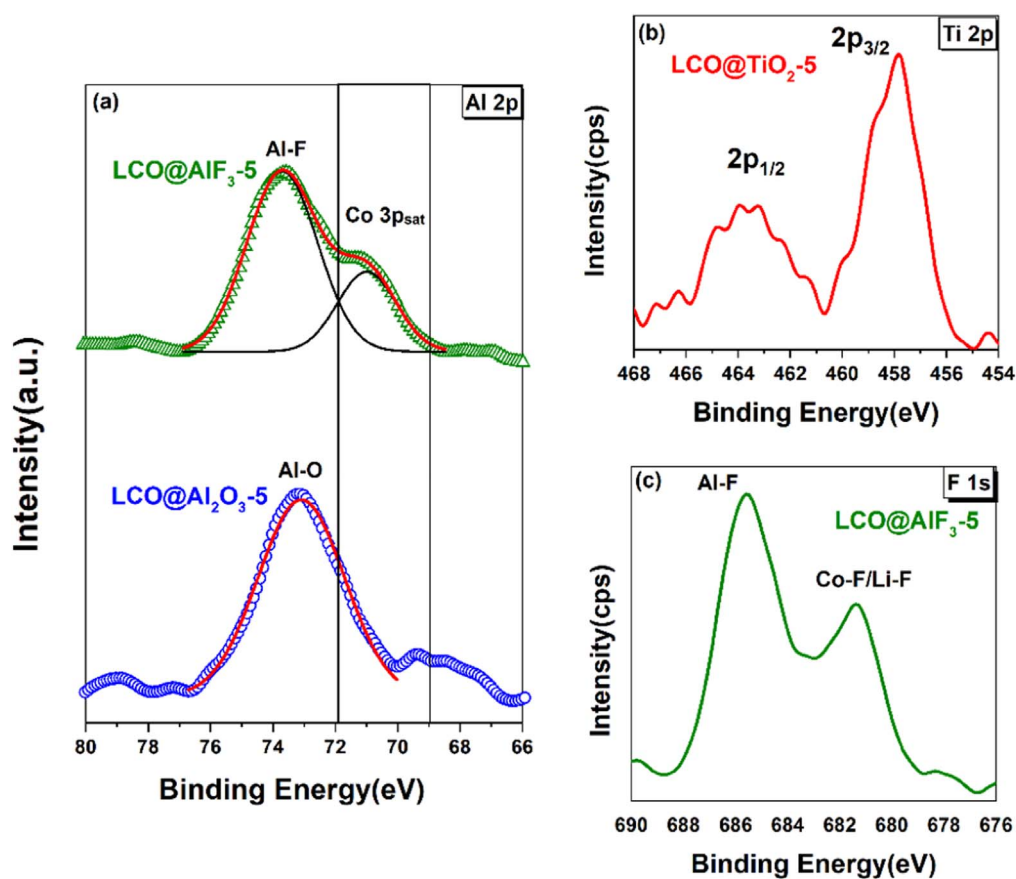


Figure 4. High resolution XPS spectra of (a) Al 2p of LCO@Al₂O₃-5 and LCO@AlF₃-5 (b) Ti 2p and (c) F 1 s of LCO@TiO₂-5 and LCO@AlF₃-5 samples respectively.

respectively [28]. There observed a peak at 282.8 eV for LCO@Al₂O₃-5 and at 281.2 eV for LCO@AlF₃-5 corresponds to Al-C bond formation [29]. Figure 3(b) evidence the presence of Co 2p_{1/2} and Co 2p_{3/2} at 794.7 eV and 779.5 eV respectively in all four samples indicating Co³⁺. Intensity of these peaks seems less for LCO@AlF₃-5 compared with others due to thicker coating. In figure 3(c), lattice oxygen O²⁻ is present at 529.1, 529.4, 529.2 and 529.3 eV for LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 respectively. Presence of peaks at around 531 eV for LCO is from M-OH bond and intensity of that peak is less for LCO@TiO₂-5 sample. Appearance of a doublet at 530.1 eV for LCO@Al₂O₃-5 attributes to the formation of O-Al and O-H bonds [15]. For LCO@Al₂O₃-5 and LCO@AlF₃-5 samples, there exist peaks at 527.3 eV and 527.5 eV respectively. It represents the adsorbed oxygen species on the surface and it is more intense for LCO@AlF₃-5 sample due to the presence of a highly electronegative F⁻ associated with a highly electropositive defective Al⁺ [30, 31]. Figure 4(a) shows the Al 2p spectra of LCO@Al₂O₃-5 as well as LCO@AlF₃-5 sample. For LCO@Al₂O₃-5, peak obtained at 73.3 eV relates to the formation of Al₂O₃ along with LiCo_{1-x}Al_xO₂. It shows that Al diffusion also happens in the LCO surface along with coating [15]. For LCO@AlF₃-5 peaks obtained at 73.8 eV emerges from Al-F bond. Also, Co 3p_{sat} peak is noticeable in both Al₂O₃ and AlF₃ coated samples at 69 eV and 71 eV respectively. Figure 4(b) shows two peaks at 463.7 and 457.8 eV signifies to Ti 2p_{1/2} and Ti 2p_{3/2} respectively. It confirms the existence of Ti in 4⁺ oxidation state [32]. F 1s spectrum of LCO@AlF₃-5 is seen in figure 4(c). Peaks at 685.6 eV and 681.3 eV signifies the presence of AlF and Co-F respectively as reported in the literature [33]. In this work, for LCO@AlF₃-5, Co-F/Li-F peak is intense possibly because of the inter-diffusion of elements from a thick AlF₃ layer on LCO. Wide survey scan and high-resolution Li 1s spectra for all samples are given in figure S5.

3.2. Electrochemical characterizations

Electrochemical studies were carried out to understand the effect of different coating chemistry and thickness on LCO at high voltages (≥ 4.5 V). Figures 5(a)–(d) shows the first-charge-discharge of LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 at different current densities of 100 mA g⁻¹, 250 mA g⁻¹, 500 mA g⁻¹ and 1000 mA g⁻¹ in a voltage window of 3.0–4.5 V. Figures 6(a)–(d) corresponds to the first cycle charge-discharge of all samples at different current densities in 3.0–4.8 V. It is seen that at 4.5 V and 4.8 V, first cycle Coulombic efficiency (ICE) of LCO was 84.6% and 84.3% respectively for a current density of 100 mA g⁻¹. At 4.5 V, both LCO@TiO₂-5 and LCO@AlF₃-5 offered an ICE of 90%. At higher voltage of 4.8 V, LCO@AlF₃-5 exhibited an ICE of 87% which is similar to LCO@TiO₂-5, ICE of 84.5%. Among all the samples, LCO@Al₂O₃-5 exhibited a high ICE of 95% and 91% at charge voltages of 4.5 V and 4.8 V respectively.

Rate capability studies were performed on bare as well as coated samples at higher voltages and is given in figure 7. It is seen from figure 7(a) that when cycled till 4.5 V, LCO could only delivered a capacity of 161.4, 141.1, 123.6 and 100.6 mAh g⁻¹ at 100, 250, 500 and 1000 mA g⁻¹ respectively. For LCO@TiO₂-5 and LCO@AlF₃-5 the capacity obtained was 173.2, 144.7, 119.3, 98.3 mAh g⁻¹ and 141.8, 128, 115.3, 98.7 mAh g⁻¹ respectively at the mentioned current densities. Among the bare and coated samples, LCO@Al₂O₃-5 exhibited an enhanced performance with specific capacities of 169.2, 156.2, 145 and 130 mAh g⁻¹ at 100, 250, 500 and 1000 mA g⁻¹ respectively. Figure 7(b) shows the rate performance of the samples at a higher voltage of 4.8 V. Obtained capacities of LCO and LCO@TiO₂-5 were 192.2, 143.2, 111.2, 66.3 mAh g⁻¹ and 194.7, 148.7, 125.3, 95.5 mAh g⁻¹ respectively. Whereas, LCO@AlF₃-5 offered discharge capacities of 173, 141, 120 and 97.3 mAh g⁻¹ at 100, 250, 500 and 1000 mA g⁻¹ respectively. Even at a higher voltage of 4.8 V, LCO@Al₂O₃-5 exhibited an excellent rate capability with 212.7, 167, 145.3 and 126.5 mAh g⁻¹ at current densities of 100, 250, 500 and 1000 mA g⁻¹ respectively. It is clearly seen from the obtained capacities that, LCO@Al₂O₃-5 sample has the ability to maintain good electrochemical performance even at high current density of 1 A g⁻¹ and a high voltage of 4.8 V. The enhanced rate capability of LCO@Al₂O₃-5 may be attributed to the co-effect of Al₂O₃ surface coating as well as Al diffusion into LCO, which was evident in the XPS results. The diffusion of Al to the LCO surface leads to lower charge-transfer resistance by minimizing the structural degradation that resulted in better capacity even at high rates.

Figure 8 indicates the cycling performance of bare and coated samples at a current density of 200 mA g⁻¹ (~ 1 C) at 4.5 V and 4.8 V. It is observed that at 4.5 V bare LCO exhibited a retention of 42.2% after 100 cycles at 200 mA g⁻¹. LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 offered 57.6%, 77.6% and 84% retention respectively. At a high voltage of 4.8 V retention of LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 were 17.1%, 10.2%, 43.3% and 46% respectively at the end of 100 cycles. It is noted that capacity fade for LCO@TiO₂-5 is more compared to even bare LCO and it says that TiO₂ coating is not enough capable of preventing surface transformation at higher voltages, which will be further discussed in detail during *ex situ* analysis. In terms of cycling stability, LCO@AlF₃-5 exhibits good cycle life at 4.5 V and 4.8 V. 1st, 25th, 50th and 100th cycle charge-discharge profile of all samples at 4.5 V as well as 4.8 V is given in figures S6 and S7 respectively. Coulombic efficiency versus cycle number of all the samples at 4.5 V and 4.8 V were shown in figure S8. Both LCO@Al₂O₃-5 and LCO@AlF₃-5 has a Coulombic efficiency of 98% over the completion of 100 cycles at higher voltage of 4.8 V. For LCO and LCO@TiO₂-5, Coulombic efficiency was so less possibly due to significant transition metal dissolution over cycling that leads to detrimental structural phase transformation. From XPS, we have seen the presence of strong Co-F bond for LCO@AlF₃-5 sample which in turn reduces the anionic activity at high voltages and thereby resulted in decreased capacity. Moreover, the thickness of AlF₃

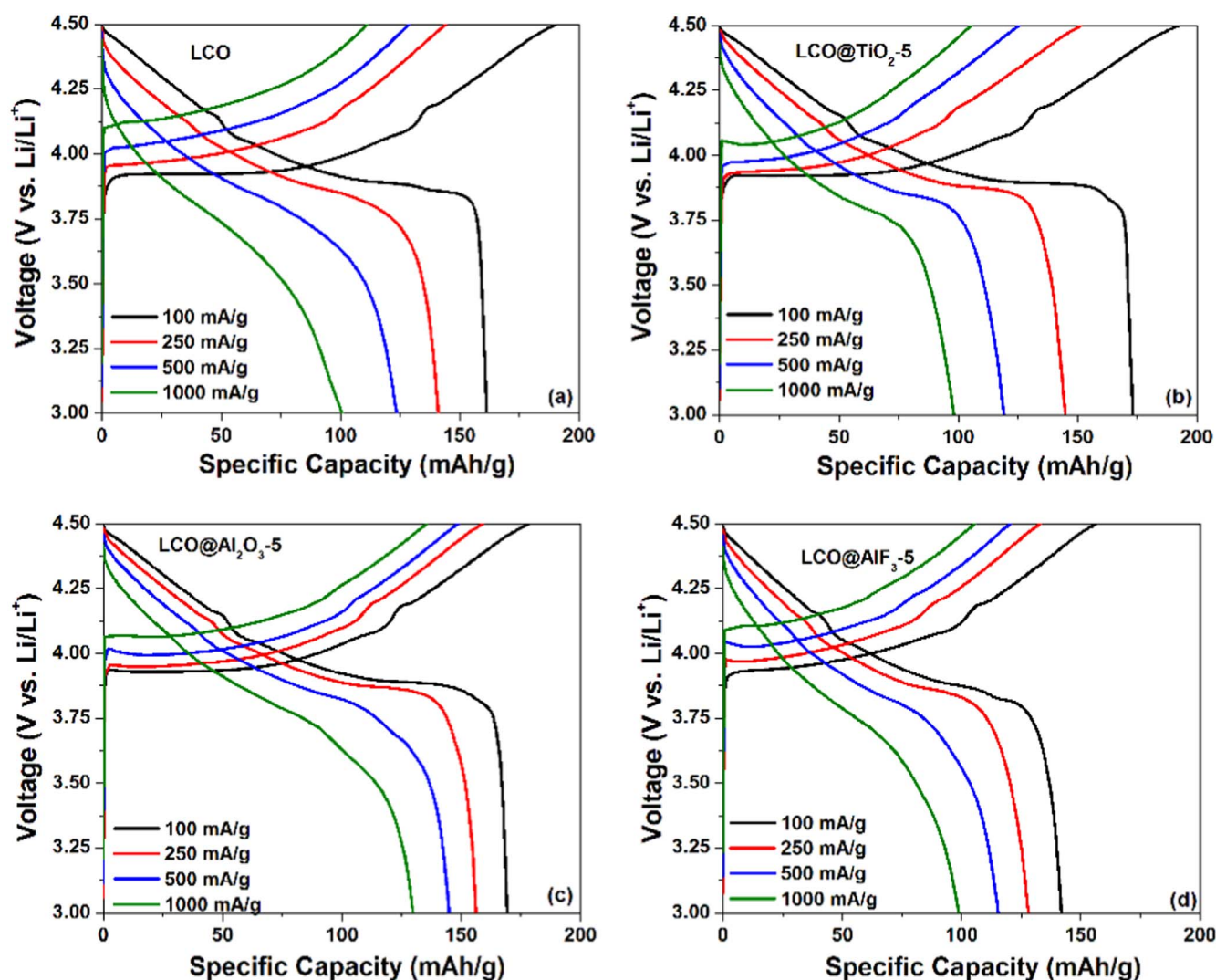


Figure 5. First cycle charge–discharge profile of (a) LCO (b) LCO@TiO₂-5 (c) LCO@Al₂O₃-5 and (d) LCO@AlF₃-5 at different current densities in 3.0–4.5 V.

layer is more than other coated samples which could be a reason for the less capacity of LCO@AlF₃-5 compared to LCO@Al₂O₃-5. There may be the possibility of AlF₃ diffusion into the surface LCO that stabilizes the cycling performance of the material, which is not able to probe through XPS due to the thicker coating layer.

Electrochemical impedance studies were conducted on bare and coated samples at four different stages of cycling at 50 mA g⁻¹ at both 4.5 V and 4.8 V to evaluate the effect of coating. EIS data was recorded at OCV, at the end of, 1st charge, 1st cycle and 10th cycle, as shown in figures S9 and S10. Tables S2 and S3 gives the estimated series resistance (R_s) and charge-transfer resistance (R_{ct}) values of all the samples at 4.5 V and 4.8 V respectively. It is observed that after 10 cycles at 4.5 V, LCO has higher R_{ct} value of 123 Ω and it is least for LCO@Al₂O₃-5 with 63.2 Ω . For all the samples, R_s value got increased from 1st cycle to 10th cycle and it could be because of the increased contact resistance or solution resistance. Over 10 cycles at 4.8 V R_{ct} values of LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 were

found to be 96, 142, 83 and 167 Ω respectively. The increased R_{ct} value of LCO@TiO₂-5 compared to LCO indicates the hindrance to proper Li⁺ diffusion in/out of the structure that resulted in poor electrochemical performance seen in figure 8. Likewise, LCO@AlF₃-5 possess high R_{ct} value compared to LCO@Al₂O₃-5 at both 4.5 V and 4.8 V. This could be possibly due to the presence of thicker layer of AlF₃ coating on the LCO surface. Presence of Co-F in AlF₃ creates hindrance for proper Li-ion diffusion through the coating layer. This resulted in less capacity of LCO@AlF₃-5 coated sample at high rates when compared with LCO@Al₂O₃-5. LCO@Al₂O₃-5 exhibited lower charge-transfer resistance compared with other samples at both 4.5 V and 4.8 V over 10 cycles. Improved diffusion kinetics of LCO@Al₂O₃-5 is ascribed to the solid solution phase formation on the material surface along with Al₂O₃ coating that created an easy path for Li-ion movement. We expect that maybe a thin layer of AlF₃ coating on LCO surface would help in enhancement of electrochemical performance at higher voltages with faster kinetics.

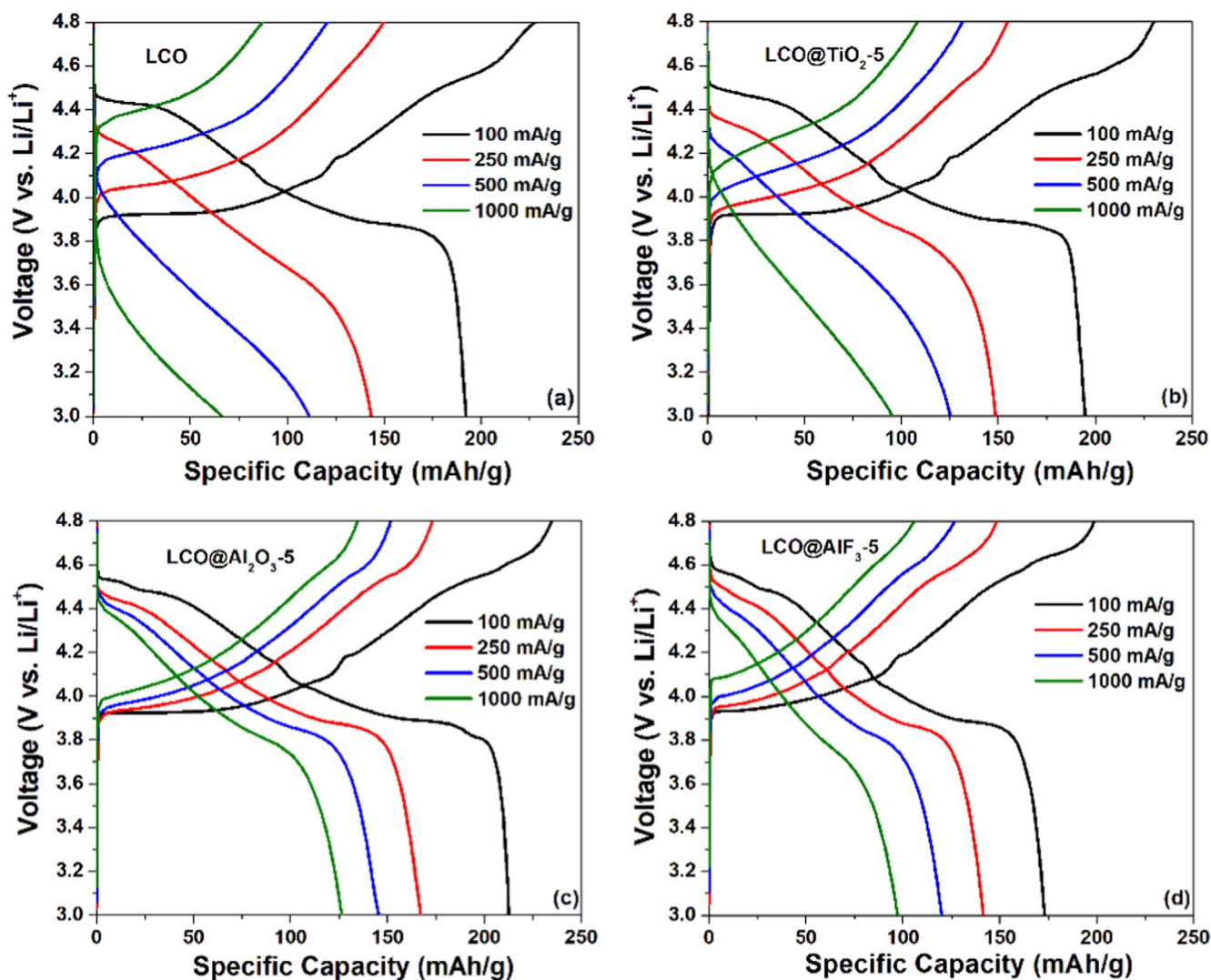


Figure 6. First cycle charge-discharge profile of (a) LCO (b) $\text{LCO@TiO}_2\text{-5}$ (c) $\text{LCO@Al}_2\text{O}_3\text{-5}$ and (d) $\text{LCO@AlF}_3\text{-5}$ at different current densities in 3.0–4.8 V.

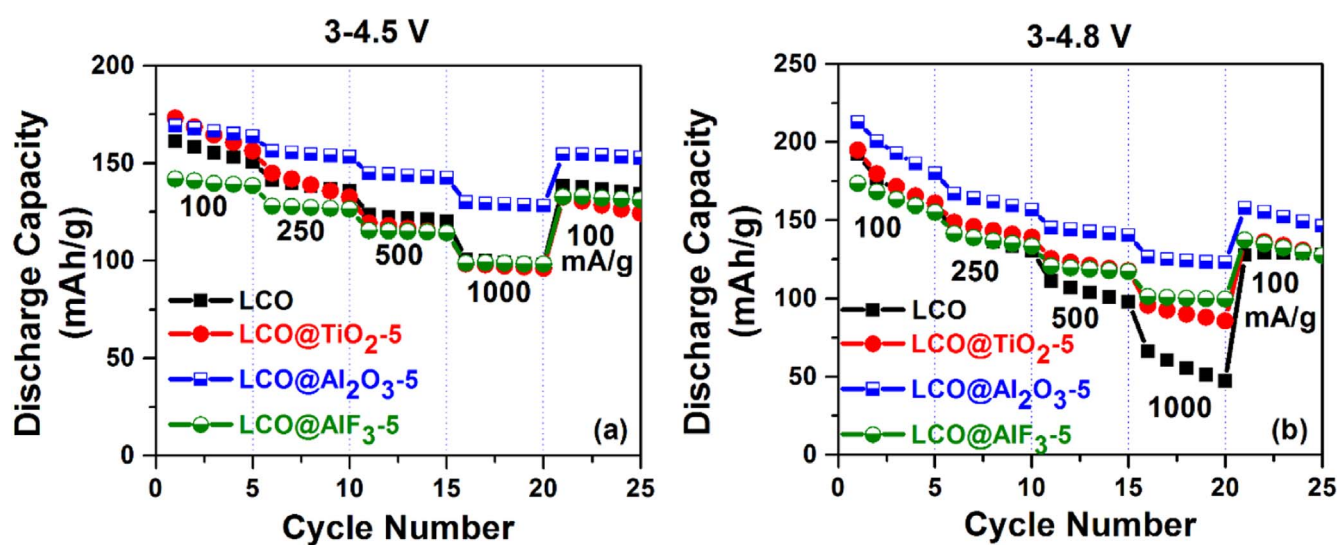


Figure 7. (a) and (b) Rate performance of LCO, $\text{LCO@TiO}_2\text{-5}$, $\text{LCO@Al}_2\text{O}_3\text{-5}$ and $\text{LCO@AlF}_3\text{-5}$ at different current densities in a voltage window of 3.0–4.5 V and 3.0–4.8 V respectively.

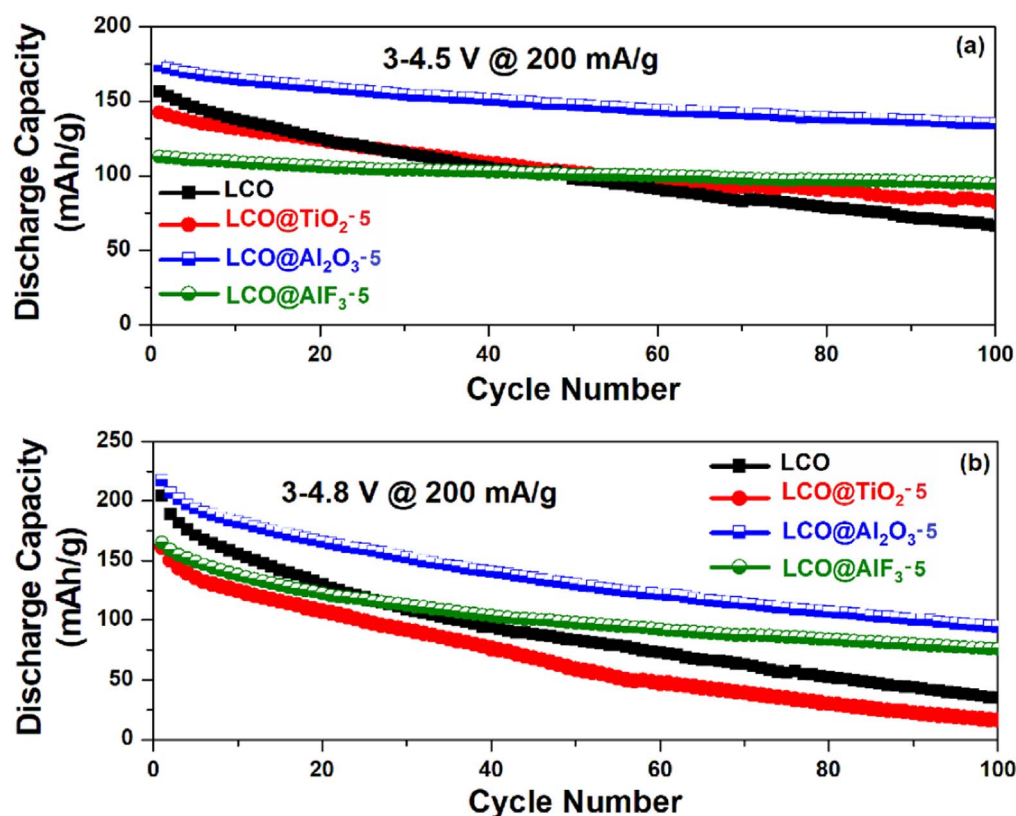


Figure 8. (a) and (b) Cycling performance of bare and coated samples at 4.5 V and 4.8 V respectively.

To evaluate our hypothesis on thickness effect, we prepared LCO samples with 1 wt% and 2 wt% AlF₃ coating. AlF₃ coated LCO samples were cycled at 200 mA g⁻¹ in a voltage window of 3–4.5 V as shown in figure S11. LCO@AlF₃-2 sample rendered high capacity and stability over 100 cycles compared to LCO as well as other weight ratios of AlF₃ coated samples. Among different weight ratios of AlF₃ coating, LCO@AlF₃-2 is selected for further studies because of its enhanced performance at 4.5 V. XRD and FESEM data of LCO@AlF₃-2 is presented in figure S12 and S13 respectively. XRD reveals the phase purity and well-crystallized nature of the material with amorphous/thin coating. FESEM indicates LCO@AlF₃-2 with a particle size of 150–200 nm. HRTEM images of LCO@AlF₃-1 and LCO@AlF₃-2 are presented in figure S14, confirms the presence of a thinner (5–7 nm and 10–12 nm respectively) AlF₃ layer on LCO surface compared to LCO@AlF₃-5 coating thickness (15–18 nm). XPS spectra of LCO@AlF₃-2 is given in figure S15. Compared with LCO@AlF₃-5, XPS spectra of LCO@AlF₃-2 remains similar which confirms the presence of AlF₃ coating on LCO surface whereas F 1s spectra differs. In LCO@AlF₃-5 sample, there exists the presence of intense Co–F peak but in LCO@AlF₃-2 sample, it is not present. This indicates the thin coating of AlF₃ over LCO surface. Figures 9(a) and (b) shows the rate performance comparison of LCO@AlF₃-2 sample with other samples at charge cutoff of 4.5 V and 4.8 V. First cycle charge–discharge profile at different current densities at both 4.5 V and 4.8 V is given in figure S16. It offers an ICE of 94% at 4.5 V and 90.5% at 4.8 V. From figure 9(a), it is observed that when

cycled at 4.5 V, LCO@AlF₃-2 delivered capacities of 165, 153, 142 and 127 mAh g⁻¹ at 100, 250, 500 and 1000 mA g⁻¹ respectively which is similar to the capacities achieved by LCO@Al₂O₃-5. At a higher voltage of 4.8 V, it delivered 182.6, 135, 113.5 and 94.4 mAh g⁻¹ at 100, 250, 500 and 1000 mA g⁻¹ respectively. When compared to LCO@Al₂O₃-5 and LCO@AlF₃-5 cycled at 4.8 V, the rate capability of LCO@AlF₃-2 is less. Based on these results, we carried out a detailed electrochemical performance comparison of LCO@Al₂O₃-5 with LCO@AlF₃-2 with the charge cutoff voltage limit as 4.5 V. Figure 9(c) show the cycling data at a current density of 200 mA g⁻¹, over 100 cycles, LCO@AlF₃-2 offered a good cycling stability with 88% retention which is higher compared to LCO@Al₂O₃-5 and moderate compared to LCO@AlF₃-5.

Considering the better cycling stability and capacity, we studied the cycle life performance of LCO@Al₂O₃-5 and LCO@AlF₃-2 at LT (–12.5 °C) and HT (55 °C) at a current density of 200 mA g⁻¹. Figure 10 represents the cycle life of LCO@Al₂O₃-5 and LCO@AlF₃-2 at different temperatures at a current density of 200 mA g⁻¹. It is seen that LCO@Al₂O₃-5 retained 76% of its initial discharge capacity over 100 cycles and LCO@AlF₃-2 retained 78% at HT. When cycled at –12.5 °C, LCO@Al₂O₃-5 exhibited better cycling stability with a retention of 72% over 100 cycles with a capacity of 108 mAh g⁻¹, whereas LCO@AlF₃-2 could only retained 61% of its initial discharge capacity. Over 100 cycles, discharge capacity of LCO@AlF₃-2 decreased from 112 mAh g⁻¹ to 66 mAh g⁻¹. In spite of good cycling

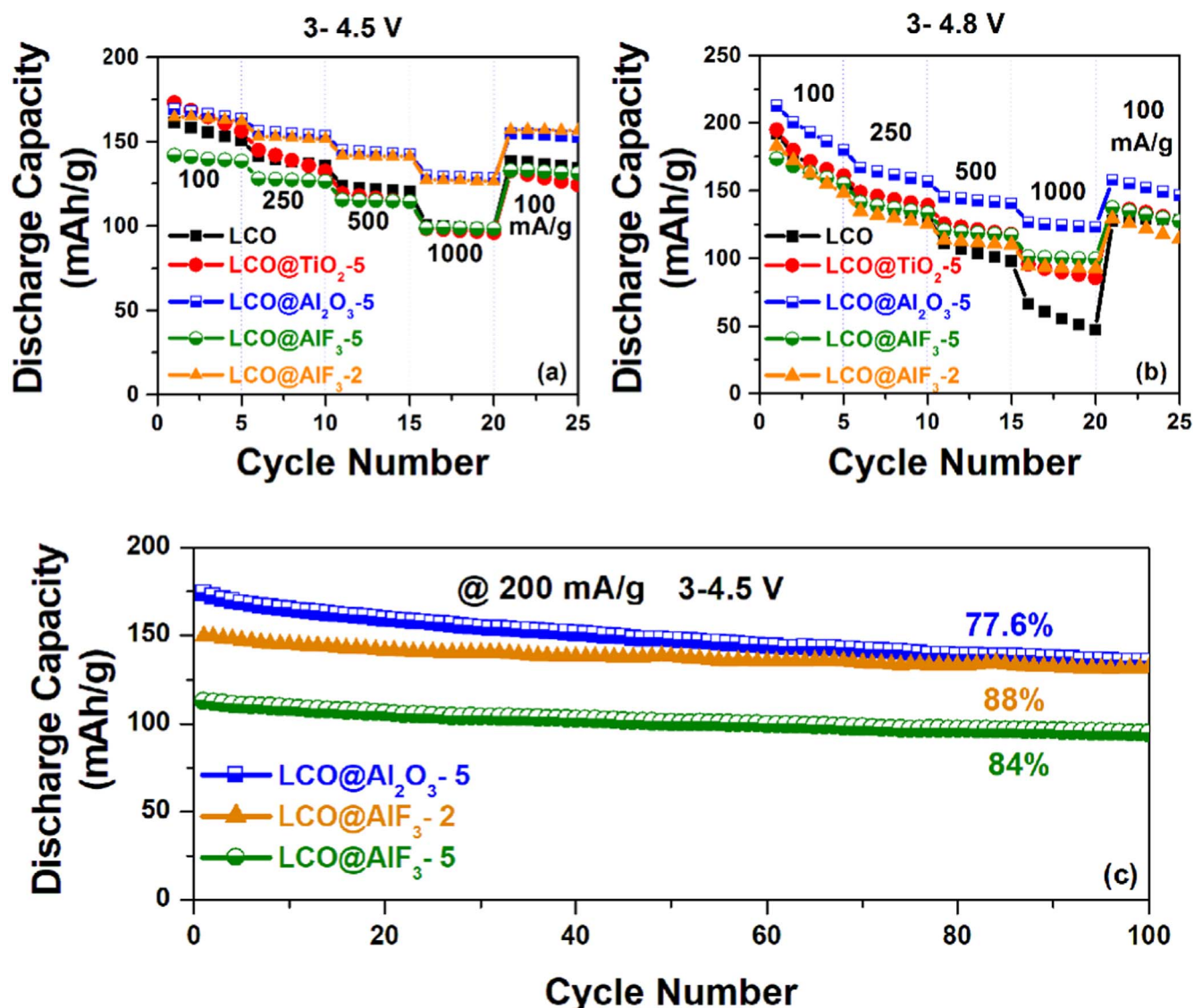


Figure 9. (a) and (b) Rate performance of LCO, LCO@TiO₂-5, LCO@Al₂O₃-5, LCO@AlF₃-5 and LCO@AlF₃-2 at different current densities in a voltage window of 3.0-4.5 V and 3.0-4.8 V respectively (c) Cycling data at 200 mA g⁻¹ in a voltage window of 3-4.5 V.

stability at RT and HT, LCO@AlF₃-2 could not perform well at LT compared to LCO@Al₂O₃-5.

In order to further explore the potential of LCO@Al₂O₃-5, we did long cycling at higher current rates both at RT and HT and data is given in figure 11. At a current rate of 5 C (1 A g⁻¹), it delivered an initial capacity of 153 mAh g⁻¹ and retained 115 mAh g⁻¹ with 75.2% retention at the end of 500 cycles. At a higher current density of 10 C, it offers 72.2% retention with a capacity of 109 mAh g⁻¹ over 500 cycles. LCO@Al₂O₃-5 outperformed among other samples even at high temperature of 55 °C and current density of 1 A g⁻¹ with 81% and 67% retention after the completion of 100 and 500 cycles respectively with a discharge capacity of 103 mAh g⁻¹. We synthesized LCO@Al₂O₃-2 to evaluate whether thin coating of Al₂O₃ can improve the electrochemical performance further. Figures S17 and S18 shows the XRD and FESEM of LCO@Al₂O₃-2 respectively. XRD reveals the crystalline structure of the sample with minor traces of Co₃O₄.

Figure S19 shows the electrochemical performance of the sample and it is seen that LCO@Al₂O₃-2 offers 95% ICE at 100 mA g⁻¹ at 4.5 V. Rate capability studies shows that it delivered 165.2, 151, 139.5 and 126 mAh g⁻¹ at 100, 250, 500 and 1000 mA g⁻¹ respectively at 4.5 V which is more or less similar to LCO@Al₂O₃-5. LCO@Al₂O₃-2 maintained 77.8% retention over 100 cycles at 200 mA g⁻¹, almost similar to LCO@Al₂O₃-5. Thereby, it is concluded that LCO@Al₂O₃-5 is the best among all other samples, which could act as a suitable cathode at various temperatures (LT, RT and HT) and higher voltages with preserving the structural stability. Inspired from a previous report [34], we carried out electrochemical testing of LCO@Al₂O₃-5 at 4.65 V to observe the performance which is a cut-off in between 4.5 and 4.8 V. Figure S20 shows the comparison of rate capability and cycling performance of LCO@Al₂O₃-5 at 4.5, 4.65 and 4.8 V. It is observed that at 100 mA g⁻¹, the electrode exhibited more capacity at 4.65 V than at 4.5 V. But at higher

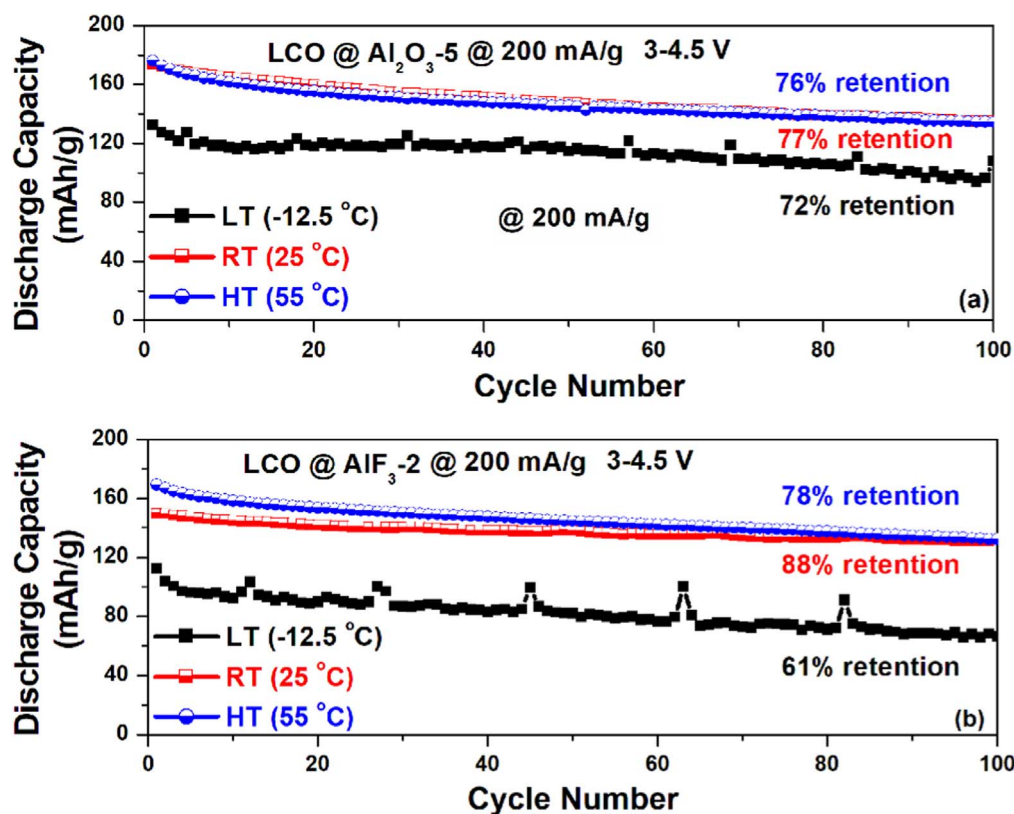


Figure 10. Cycling data of (a) LCO@Al₂O₃-5 and (b) LCO@AlF₃-2 at different temperatures respectively.

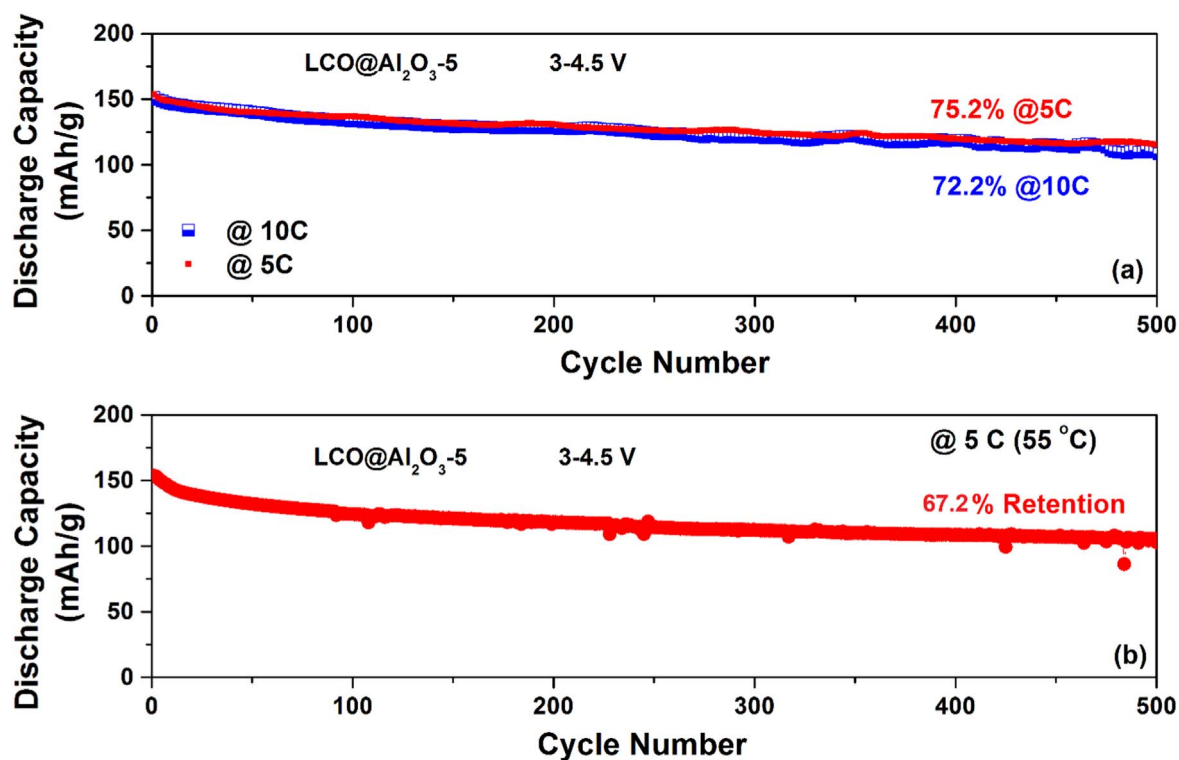


Figure 11. (a) Long cycling of LCO@Al₂O₃-5 at current rates of 5 C and 10 C at RT (b) Cycling data at 55 °C.

current densities, LCO@Al₂O₃-5 delivered almost same capacity at 4.5 and 4.8 V whereas it was less for 4.65 V electrode. It is observed that the capacity retention for the cell tested with 4.65 V cut-off is poor than that of the 4.8 V cut-off cell. Seong *et al* [34] demonstrated a similar trend for their LiCoO₂ samples, their 4.8 V cut-off cell delivered better capacity retention than the 4.6 or 4.7 V cell. However, their AlPO₄ coated LCO cell delivered better capacity retention at 4.6 V than at 4.8 V cut-off which is different to our observations. The mechanism for the LCO sample and AlPO₄ coated LCO sample performance was reported to be different. In the present work, LCO@Al₂O₃-5 exhibited 77.6%, 40.7% and 43.4% retention at 4.5, 4.65 and 4.8 V respectively at the end of 100 cycles at 200 mA g⁻¹. Cycling stability of LCO@Al₂O₃-5 at 4.65 V is less compared to 4.8 V cut-off. The difference compared with [34] AlPO₄ coated LCO samples could be due to the particle size difference and high current rate. Also, in the present study more delithiation during first charge could be another reason for the lesser stability at 4.65 V.

Table 1 shows a literature survey of previous studies reported related to the effect of surface modification of LCO on enhancement of electrochemical performance at high voltages. It is to be noted that our work is comparable to other reports with better performance and there are only very few reports on LCO at 4.8 V so far. Importantly, there is not even a single report on surface modified LCO showing 500 cycles at current rates of 5 C (1 A g⁻¹) and 10 C (2 A g⁻¹) at 4.5 V. Also considering the low temperature and high temperature electrochemical performances, our LCO@Al₂O₃-5 stands top of other literatures reported till to date.

3.3. Ex situ XRD and Raman analysis

For a better understanding of the correlation between electrochemical performance and structural changes at different stages of cycling, we have performed *ex situ* XRD and *ex situ* Raman analysis at the end of 1st charge, 1st cycle and 10th cycle at 50 mA g⁻¹. *Ex situ* XRD spectra of all sample electrodes at 4.5 V is given in figure S21. Figure 12(a) shows the magnified XRD characteristic (003), (101) and (104) peaks of LCO after 1st charge, 1st cycle and at the end of 10th cycle at 4.5 V. After the initial charge, (003) peak vanishes and it appeared after 1st cycle at 18.6°. At the end of 10th cycle, the (003) peak shifted to higher angle with lesser intensity compared to 1st cycle, indicating lattice compression and structural degradation. This is consistent with a noticeable shift in (101) and (104) peaks to higher angles after 10th cycle compared to 1st cycle and Co₃O₄ peaks are present in all the samples. It may be noted that peak shift to higher angles is typically attributed to the transition metal-ion migration to lithium layer that contributes to significant reduction in capacity at higher current rates [49]. In figure 12(b), for LCO@TiO₂-5 cycled at 4.5 V, peak values obtained after 1st cycle were 18.7, 37.1 and 45.1 for (003), (101) and (104) respectively. But, at the end of 10th cycle it got shifted to lower angles without much peak intensity variation. Similar peak shifts were observed for LCO@Al₂O₃-5 electrodes in

figure 12(c). Peak shifts occurring to lower angles indicates the increased inter-planar spacing of (003) slab. This favors faster Li⁺ diffusion and thereby enhanced rate capability of the material. Figure 12(d) indicates the (003), (101) and (104) peak positions and intensity variation of cycled LCO@AlF₃-5 electrodes. It is noted that, all peaks at different stages of cycling were aligned in the same position without any peak shifts. Also, peak intensity increased after 10th cycle with respect to 1st cycle. No significant XRD peaks were observed at the end of 1st charge for all these samples.

Ex situ XRD spectra of all samples at 4.8 V are given in figure S22. Figure 13(a) shows the magnified XRD spectra of LCO electrodes at charged state, 1st and 10th cycle conditions at 4.8 V. Consistent to 4.5 V cycled LCO, all peaks recorded at 10th cycle were shifted to higher angle when compared to peak positions at 1st cycle. At charged state of 4.5 V, small traces of (101) peak was present whereas at 4.8 V, it got diminished further. In case of LCO@TiO₂-5, (101) and (104) got completely vanished after 10 cycles as seen in figure 13(b). This implies the irreversible structural transformation happened to the material at 4.8 V and it can be correlated to the poor electrochemical performance exhibited (figure 8). LCO@Al₂O₃-5 and LCO@AlF₃-5 electrodes cycled up to 4.8 V, *ex situ* XRD data is shown in figures 13(c) and (d) respectively. In both the samples, there is no peak shift observed during different stages. In LCO@Al₂O₃-5, there emerges a doublet around (003) peak region, which possibly indicates two different *c*-axis lattice parameters in the bulk and at the surface. Also, Co₃O₄ peak intensity got increased compared to 4.5 V. For LCO@AlF₃-5 electrodes, similar to the XRD data seen at 4.5 V, all the peak positions and intensity remains almost same at all different stages of cycling at 4.8 V, indicates the structural stability of the sample compared with others. Due to the presence of a thicker AlF₃ coating, less lithium was allowed to move in and out of the material resulted in structural maintenance with better cycling stability and less capacity compared to LCO@Al₂O₃-5 (figure 8). For a further confirmation on structural changes during cycling, we conducted *ex situ* Raman analysis on electrodes cycled at 4.5 V as well as 4.8 V under same conditions as the *ex situ* XRD analysis.

Figure 14(a) depicts the *ex situ* Raman spectra of LCO cycled at 4.5 V. After 1st charge, E_g peak and Co₃O₄ peak is seems to be intense and peaks have been shifted to lower frequency. But after 1st cycle there occurs a higher frequency shift, material structure is retained with the existence of both E_g and A_{1g} peak with a less intense Co₃O₄ peak. Upon further cycling, Co₃O₄ peak dominated over the main peaks of LCO indicating the structural distortion. Raman spectra of cycled LCO@TiO₂-5 electrodes at 4.5 V are shown in figure 14(b). At the charged state, intensity of Co₃O₄ peak is more compared to the bare LCO. Also there exists the presence of E_g and A_{1g} peaks along with small traces of Co₃O₄ after 10th cycle. In LCO@Al₂O₃-5 cycled electrodes Raman data, there observed a clear lower frequency shift of E_g and A_{1g} peaks after 1st cycle and 10th cycle compared with initial charged state. Also, there exists an intense Co₃O₄ peak after 10 cycles. From literatures, it is

Table 1. Literature based on electrochemical performance of LCO at higher voltages.

Material (Coating Process)	Voltage (V)	Current density (mA g ⁻¹)	Capacity (mAh g ⁻¹)	Retention (%)	References
LCO@AlF ₃ (Wet-chemical process)	3–4.5	160 480 800	185 183 178	97.7% at 80 mA g ⁻¹ after 50 cycles	[35]
LCO@AlF ₃ (Wet-chemical process)	3–4.5	160 480 800	185 183 180	94.4% at 80 mA g ⁻¹ after 50 cycles	[36]
LCO@Li[Li _{0.2} Mn _{0.6} Ni _{0.2}]O ₂ (Wet-chemical process)	3–4.5	150	169	94.7% at 30 mA g ⁻¹ after 100 cycles	[37]
LCO@BT (Wet-chemical process)	3–4.5	300 100 200 400 600 1000	167 175 162 155 125 100	90.29% at 40 mA g ⁻¹ after 100 cycles	[19]
LCO@AZO (Wet-grinding process)	3–4.5	92.5 185 370 740	175 160 150 126	80% at 38 mA g ⁻¹ after 650 cycles	[38]
LCO@Al ₂ O ₃ (Wet-chemical process)	3–4.5	18	173	92.4% at 18 mA g ⁻¹ after 50 cycles	[39]
LCO@ZnO (Radio frequency magnetron sputtering)	3–4.5	140	173	77% at 28 mA g ⁻¹ after 200 cycles	[40]
LCO@MgF ₂ (Wet-chemical process)	3–4.5	280 560 1400 137 274 822 1370	156 133 106 162 153 139 115	80% at 54.8 mA g ⁻¹ after 50 cycles	[20]
LCO@Li ₃ VO ₄ (Wet-chemical process)	3–4.5	120 250 500 600 1200	150 141 133 128 115	85% at 30 mA g ⁻¹ after 100 cycles	[41]
LCO@MgAl ₂ O ₄ (Wet-chemical process)	3–4.7 3–4.5	— 160 320 800	— 179 170 158	60% at 30 mA g ⁻¹ after 50 cycles 96.8% at 160 mA g ⁻¹ after 70 cycles	[42]
LCO@Al ₂ O ₃ (Ball milling process)	3.7–4.5	20	176	63.5% at 20 mA g ⁻¹ after 500 cycles	[43]
LCO@Al ₂ O ₃ (Wet-chemical process)	3–4.5	140 280 700	195 180 160	83% at 140 mA g ⁻¹ after 500 cycles	[15]

Table 1. (Continued.)

Material (Coating Process)	Voltage (V)	Current density (mA g ⁻¹)	Capacity (mAh g ⁻¹)	Retention (%)	References
LAF-LCO (Wet-chemical process)	3–4.7	1400	130	24% at 140 mA g ⁻¹ after 500 cycles	[44]
		140	130		
		280	125		
	3–4.6	700	110	89.1% at 27.4 mA g ⁻¹ after 100 cycles	[45]
		1400	90		
LCO@LiAlO ₂ (Atomic layer deposition)	3.3–4.7	137	200	94.7% at 50 mA g ⁻¹ after 50 cycles	[46]
		274	175		
		822	90		
	3–4.8	100	115	66% at 140 mA g ⁻¹ after 110 cycles	[47]
		14	250		
LCO@AlPO ₄ (Wet-chemical process)	3–4.8	—	—	52% at 140 mA g ⁻¹ (from 5 th cycle) after 50 cycles	[48]
LCO@AlPO ₄ (Wet-chemical process)	3–4.8	—	—	78.9% at 140 mA g ⁻¹ (from 5 th cycle) after 50 cycles	[49]
LCO@LZO (Wet-chemical process)	3–4.5	100	162	85.2% at 1 A g ⁻¹ after 100 cycles 71.3% at 1 A g ⁻¹ after 100 cycles at 55 °C	
LCO@LPO (Radio frequency magnetron sputtering)	3–4.5	200	155	79.3% at 140 mA g ⁻¹ after 100 cycles 78.2% at 140 mA g ⁻¹ after 100 cycles at 50 °C	[50]
		400	144		
		1000	128		
	3–4.6	140	180	88.3% at 137 mA g ⁻¹ after 100 cycles 72.9% at 137 mA g ⁻¹ after 100 cycles at 45 °C	[51]
		280	170		
LCO@LATP (Ball milling process)	3–4.6	560	158	88.6% at 137 mA g ⁻¹ after 200 cycles 72.9% at 137 mA g ⁻¹ after 200 cycles at 45 °C	[52]
		1120	140		
		137	197		
	3–4.6	274	181	77.6% at 200 mA g ⁻¹ and 88.9% at 1 A g ⁻¹ after 100 cycles 75.2% at 1 A g ⁻¹ and 72.2% at 2 A g ⁻¹ after 500 cycles	Present work
		548	156		
LCO@Al ₂ O ₃ -5 (Wet-chemical process)	3–4.5 RT	1370	118	72% at 200 mA g ⁻¹ after 100 cycles 67% at 1 A g ⁻¹ after 500 cycles	
		137	198		
		274	182		
	–12.5 °C	548	175	76% at 200 mA g ⁻¹ after 100 cycles and 67% at 1 A g ⁻¹ after 500 cycles	
		822	168		
	55 °C	1370	149		
		100	169		
		250	156		
		500	145		
		1000	130		

Table 1. (Continued.)

Material (Coating Process)	Voltage (V)	Current density (mA g ⁻¹)	Capacity (mAh g ⁻¹)	Retention (%)	References
LCO@AlF ₃ -2 (Wet-chemical process)	3–4.8	1000	154	60% and 43.3% after 50 and 100 cycles at 200 mA g ⁻¹	
		100	213		
		250	156		
		500	145		
		1000	127		
	3–4.5 RT	100	164	88% at 200 mA g ⁻¹ after 100 cycles	
		250	153		
		500	142		
	–12.5 °C 55 °C	1000	127	61% at 200 mA g ⁻¹ after 100 cycles 78% at 200 mA g ⁻¹ after 100 cycles	
		200	112		
		200	169		

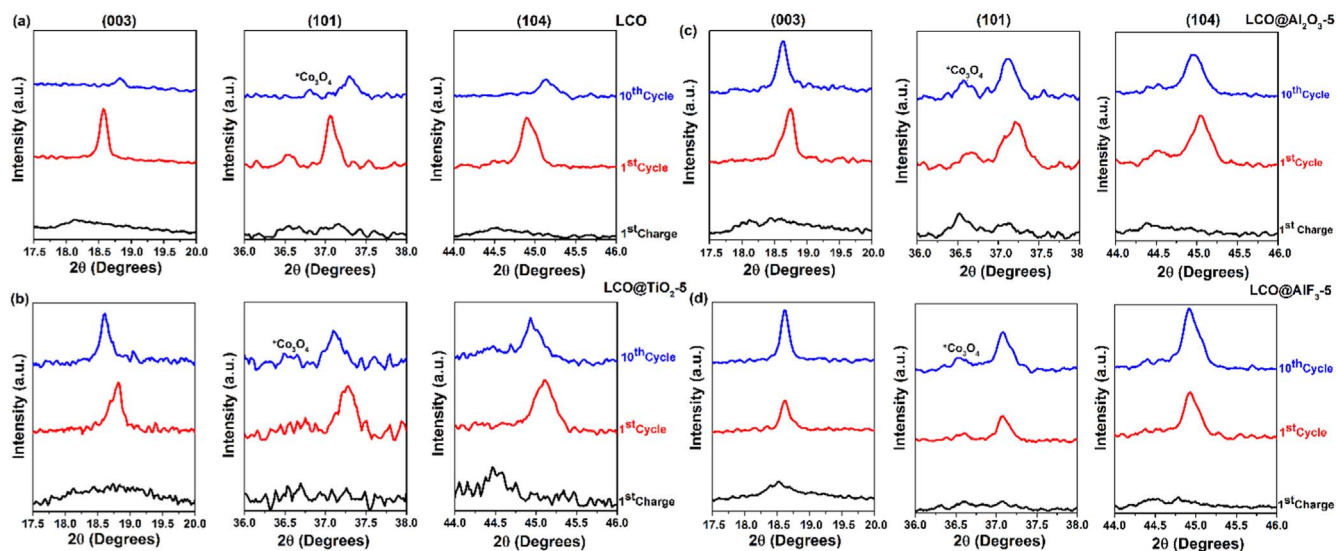


Figure 12. *Ex situ* XRD data of (a) LCO, (b) LCO@TiO₂-5, (c) LCO@Al₂O₃-5 and (d) LCO@AlF₃-5 at different stages of cycling in 3–4.5 V at 50 mA g⁻¹.

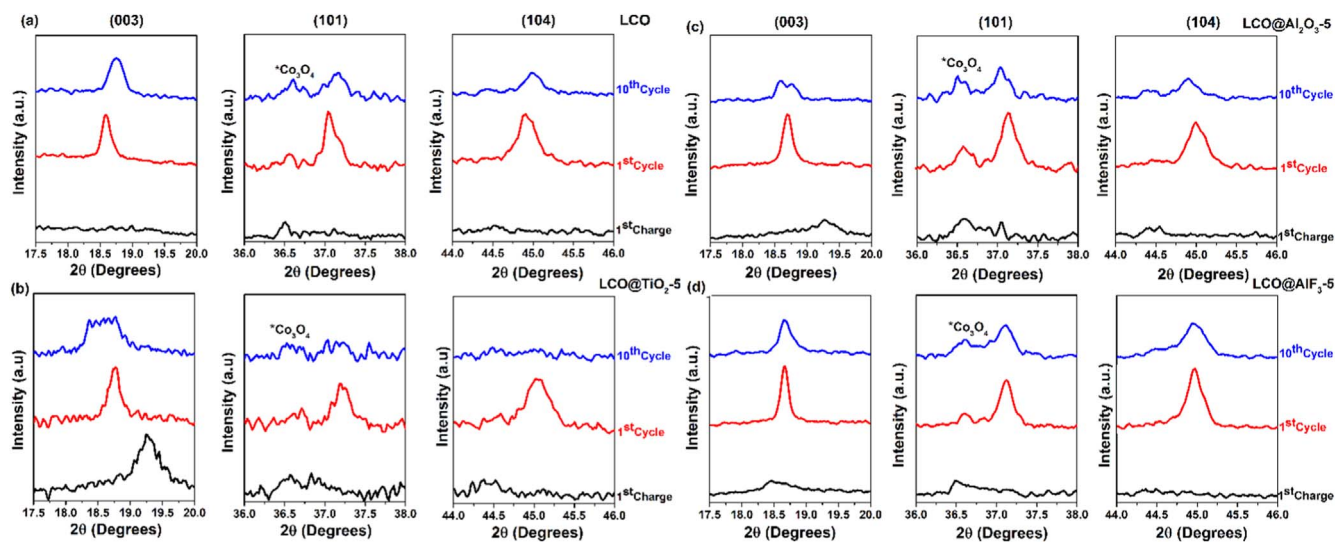


Figure 13. *Ex situ* XRD data of (a) LCO, (b) LCO@TiO₂-5, (c) LCO@Al₂O₃-5 and (d) LCO@AlF₃-5 at different stages of cycling in 3–4.8 V at 50 mA g⁻¹.

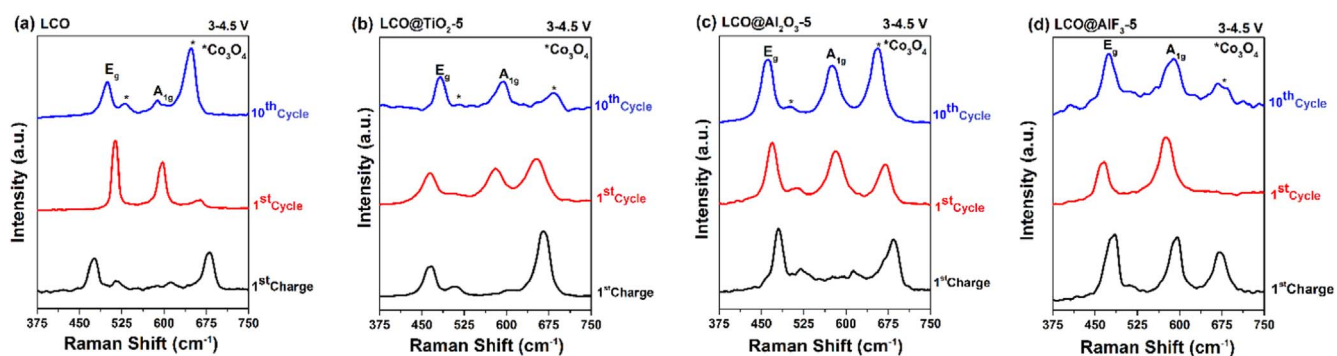


Figure 14. *Ex situ* Raman spectra of (a)–(d) LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 respectively at 3–4.5 V.

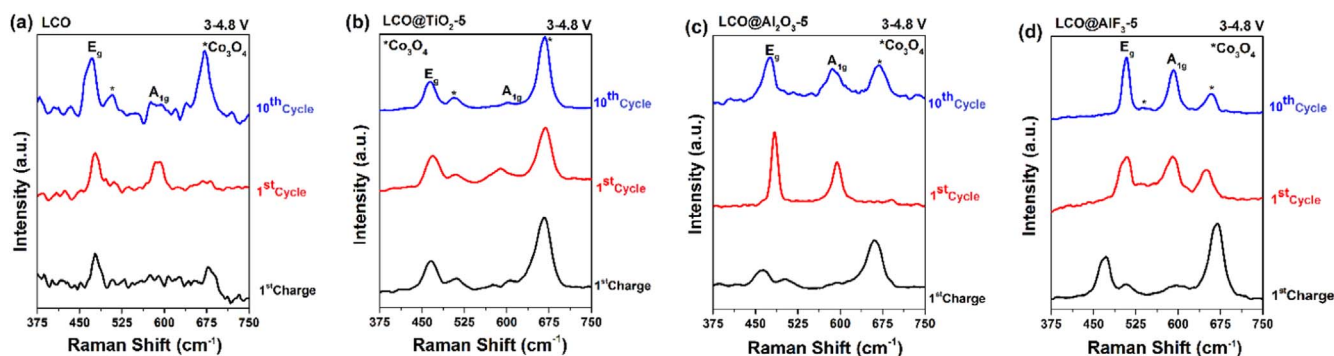


Figure 15. *Ex situ* Raman spectra of (a)–(d) LCO, LCO@TiO₂-5, LCO@Al₂O₃-5 and LCO@AlF₃-5 respectively at 3–4.8 V.

noted that lower frequency shift can be connected with lower Li content in the structure. Maximum reversible utilization of Li⁺ in LCO@Al₂O₃-5 sample resulted in high capacity even at higher rates and voltages compared with other samples (figure 7). Looking into figure 14(d), it is seen that for only LCO@AlF₃-5 sample, at charged state there exist both E_g and A_{1g} peaks indicating less lithium deintercalation. The material structure is well maintained after 1st cycle and 10th cycle with the characteristic peaks and less intense Co₃O₄ peak. This behavior can be well correlated to the *ex situ* XRD data and also the lesser capacity of the material. Figures 15(a) and (b) indicates the *ex situ* Raman of LCO and LCO@TiO₂-5 at 4.8 V respectively. It is observed that for LCO@TiO₂-5 at 10th cycle, A_{1g} peak got almost vanished with the presence of a diminished E_g peak, whereas for LCO both peaks were present. This states the reason for the poor electrochemical performance of the material compared to bare LCO at 4.8 V, which is been derived from irreversible structural transformation. In figure 15(c) for LCO@Al₂O₃-5, it is seen that peak positions got shifted to lower frequency with less intensity at 10th cycle compared to 1st cycle with *c*-axis lattice expansion. At 4.5 V, there exists Co₃O₄ peak after 1st and 10th cycle, which is expected to be present for 4.8 V cycled electrodes also. Raman spectra were recorded at several spots of LCO@Al₂O₃-5 4.8 V cycled electrode, but still Co₃O₄ peak was missing for the data at the end of 1st cycle. At this moment, no clear explanation is available for this behavior. Figure 15(d) shows the LCO@AlF₃-5 cycled electrode Raman data at 4.8 V. At charged state, E_g peak is present along with an intense Co₃O₄ peak. After 1st cycle A_{1g} peak appeared along with E_g and Co₃O₄ peaks. At the end of 10 cycles, there observed E_g and A_{1g} peaks along with small traces of Co₃O₄. Sharp and intense characteristic peaks of LCO without any lower frequency shifts present in the AlF₃ coated samples indicates the structural stability even at higher voltage of 4.8 V, which can be correlated to the *ex situ* XRD discussion. Thereby, it is concluded that the enhanced electrochemical performance of LCO@Al₂O₃-5 is attributed to the structural stability of the material with minimal surface transformations at higher voltages.

4. Conclusion

In this work, we adopted electrode-electrolyte engineering strategy on LCO with the aid of different coating chemistries and thickness. The chemistries include TiO₂, Al₂O₃ and AlF₃ with varying thickness to understand their effect at higher charge cutoff voltage of LCO (≥ 4.5 V). Structural characterization revealed the phase purity and crystallinity of the bare and engineered LCO. Morphological and surface chemical analysis evidenced the presence of various coatings over LCO with different thickness. Coating layer thickness obtained were in a range of 1–2 nm, 10–12 nm and 15–18 nm for TiO₂-5, Al₂O₃-5 and AlF₃-5 coated samples respectively. It is observed that LCO@Al₂O₃-5 delivered an enhanced capacity of 169.2 and 212.7 mAh g⁻¹, whereas LCO could only exhibit 161.4 and 192.2 mAh g⁻¹ at 100 mA g⁻¹ at 4.5 V and 4.8 V respectively. In terms of cycling stability, LCO@AlF₃-5 offered 84% retention over 100 cycles at 200 mA g⁻¹ which is more compared to bare and other coated samples at 4.5 V. Due to the presence of strong Co–F bond derived from the increased coating layer thickness of LCO@AlF₃-5 sample reduces the anionic activity at high voltages and thereby resulted in decreased capacity compared to LCO@Al₂O₃-5. Impedance analysis states the lower charge transfer resistance of LCO@Al₂O₃-5 that improved the rate capability through a stabilized electrode-electrolyte interface. Wide temperature cycling performance of both LCO@Al₂O₃-5 and LCO@AlF₃-2 were conducted at 4.5 V, 200 mA g⁻¹. At –12.5 °C, LCO@Al₂O₃-5 rendered 72% retention at the end of 100 cycles with a capacity of 108 mAh g⁻¹, whereas LCO@AlF₃-2 could only retained 61% with 66 mAh g⁻¹. Interestingly, when cycled at 10 C, LCO@Al₂O₃-5 exhibited 72% capacity retention at the end of 500 cycles for 4.5 V charge cutoff. Also at 55 °C, it retained 67% capacity at the end of 500 cycles at 5 C. At higher voltage of 4.8 V, LCO@Al₂O₃-5 exhibited 213 mAh g⁻¹ at 100 mA g⁻¹ typically a high value compared to the literatures reported for 4.8 V charge cutoff. *Ex situ* XRD and *ex situ* Raman analysis reveals the structural stability of LCO@Al₂O₃-5 at 4.5 V as well as 4.8 V with minimal surface transformations which can be well correlated to the enhanced performance of LCO@Al₂O₃-5 at higher current rates and wide temperature range. It is concluded that Al₂O₃ coating

with controlled thickness could act as an effective protection layer at the electrode-electrolyte interface of LCO and inhibit the irreversible structural phase transformations at higher voltages beyond 4.2 V. We strongly recommend the necessity of further modification of LCO@Al₂O₃-5 to enhance its cycling stability and energy density at higher voltages, beyond 4.5 V so that it can be uplifted for future high energy applications. We believe that this work would give new insights to the role of different coating chemistry and their dependence on thickness for the high voltage structural stability of LCO at wide climatic conditions.

Acknowledgments

DS acknowledges SERB, Govt. of India for awarding Ramanujan Fellowship (Ref: SB/S2/RJN-100/2014) and financial support to SSJ. Infrastructural support from Amrita Vishwa Vidyapeetham is also acknowledged. Authors acknowledge the XRD and HRTEM characterizations carried out at DST-SAIF, Cochin and PSG Tech, Coimbatore.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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