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INCREASED CYCLING PERFORMANCE OF LI-ION BATTERIES BY PHOSPHORIC ACID MODIFIED LiNi0.5Mn1.5O4 CATHODES IN THE PRESENCE OF LITHIUM BIS(OXALATO)BORATE

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INCREASED CYCLING PERFORMANCE OF LI-ION BATTERIES BY PHOSPHORIC ACID MODIFIED $LiNi_{0.5}Mn_{1.5}O_4$ CATHODES IN THE PRESENCE OF LITHIUM BIS(OXALATO)BORATE

BY

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ABSTRACT

Lithium-ion batteries (LIB) are emerging as the energy storage device of choice for vast variety of applications including electric vehicles (EV) and hybrid electric vehicles (HEV). High energy density batteries are in demand to power EVs. The best way to achieve this is the use of high voltage materials. Among all the cathode materials available for LIBs, $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) with a voltage of 4.75 vs Li/Li^+ and a theoretical capacity of 147 mAh/g shows superior properties for high voltage applications. In this study, we used phosphoric acid (PA) modified LNMO electrodes and lithium bis-(oxalato)borate (LiBOB) electrolyte additive separately and together to investigate the cell performance. The cycling data suggested that the PA modification of LNMO significantly improves the performance of LNMO/graphite full cells, which is further enhanced by LiBOB additive in the electrolyte. The metal ion concentrations obtained through ICP-MS studies performed on harvested anodes from cycled cells reveal relatively low levels of manganese and nickel deposited on the anode for PA modified LNMO and cells with LiBOB. The improvement in electrochemical performance is directly related to the reduction in transition metal dissolution. The surface analytical techniques FTIR and XPS have also been performed to further investigate the performance improvement by PA modification and LiBOB.

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I would like to express my gratitude to my advisor, Professor Brett Lucht for his patience and guidance throughout my graduate career. I am grateful to Dr. Nina Laszczynski and Dr. Sunhyung Jurng for all the fruitful discussions that lead me to the correct conclusions and Lucht research group for all the support and encouragement. I must thank everyone who were involved in this project from Helmholtz Institute Ulm, Germany. I would also like to thank Professor Brenton DeBoef, Professor Arijith Bose and Professor David Heskett in my committee for their time and their help.

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PREFACE

The thesis is written in manuscript format. Chapter 1 is an introduction to lithium ion batteries. Chapter 2 is in preparation for publication

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CHAPTER 1

INTRODUCTION

Background

World’s current energy requirement is mainly dependent on non-renewable energy sources such as fossil fuel which is not equally distributed geographically. Fossil fuel increase the CO_2 emission and hence the global warming. Due to these environmental and economic issues a different source of energy is in high demand. Lithium ion batteries (LIB) provide solutions for all above problems. After the first commercialization of LIB in 1991 it has become an effective energy storage.[1-3]

Lithium is the smallest (cationic radii is 0.76 Å) and the lightest (6.94 g/mol) alkali metal. Hence it has higher volumetric (2062 mAh/cm^3) and gravimetric (3862 mAh/g) capacities. Light weight, higher energy and power densities of LIB make them energy source of choice in most portable consumer electronics and more importantly in full/hybrid/plug-in electric vehicles (EV/HEV/PHEV). Further LIB are also useful in storing the energy yields through the renewable sources such as wind and solar power. The state of art LIB are usually a combination of graphite anode and $LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ or $LiMn_2O_4$ as cathode.[1-4]

Working Principle of LIB

The main components of LIB are a positive electrode, a negative electrode and an electrolyte. Apart from these components, LIB usually has a separator to prevent the short circuit of the battery by insulating the two electrodes. Figure 1.1 is the schematic representation of the typical working principle of LIB (discharging of the battery). This battery consists of a graphite anode and lithium metal oxide cathode.

The operating principle is intercalation and deintercalation. During the charging process, upon application of a voltage Li^+ ions are extracted from the lithium transition metal oxide (cathode) move through the electrolyte and inserted into the graphene structure. During discharging, battery goes through the reversible process spontaneously when the two ends are connected through an external circuit. At the same time electrons flow from anode to cathode through the external circuit

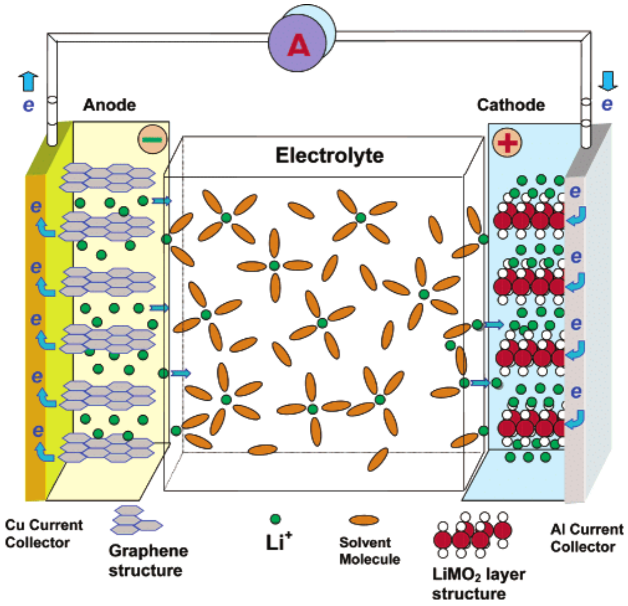

Figure 1.1: Schematic representation of a typical LIB working principle.[5]

During the charge step Li^+ ions travels from $LiMO_2$ cathode (oxidation occurs) to the anode (reduction occurs) through the electrolyte. The electrons lost from the cathode during oxidation travel through the external circuit. The reverse process spontaneously occurs during the discharge.[1, 3, 6] (reactions I and II)

$$C_6 + xe^- + xLi^+ \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_xC_6 \qquad \text{I}$$

$$LiMO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_{1-x}MO_2 + xe^- + xLi^+ \qquad \text{II}$$

Cathode

Cathode is the positive electrode and usually the Li ion source. More often cathode is a transition metal oxide and transition metal oxides are of three types. Layered, spinel and olivine (Figure 1.2). The first transition metal oxide introduced is layered $LiCoO_2$ (LCO) which was. In LCO cobalt oxide and lithium lies as alternating layers. The specific capacity of LCO is 145 $mAhg^{-1}$ and working potential is 3.9 V (vs Li/Li^+). However, LCO is expensive due to the higher cost of Co and when LCO is heated above 200 ^{0}C it exothermally releases oxygen leading to thermal hazards. Less expensive layered materials are also produced by substituting Co with much cheaper metal ions such as Ni and Mn. Eg: NCM

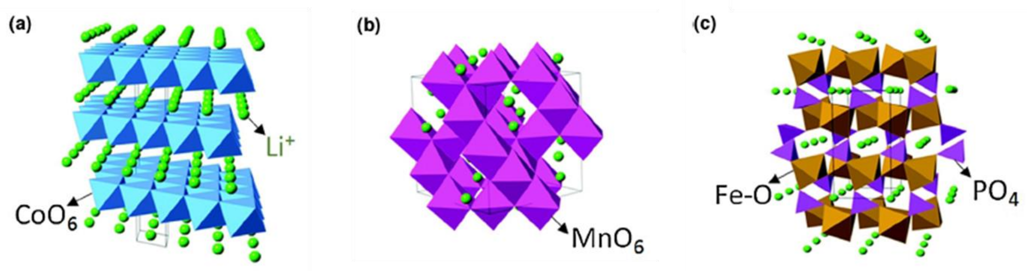

Figure 1.2: (a) Layered ($LiCoO_2$), (b) spinel ($Li_2Mn_2O_4$) and (c) olivine ($LiFePO_4$) crystal structures[1]

Compared to LCO spinel $Li_2Mn_2O_4$ (LMO) is less expensive. In this spinel structure Li and Mn occupies tetrahedral and octahedral sites respectively. LMO however is not capable of achieving long term cycling. This is mainly attributed to the Mn ion dissolution and irreversible side reactions with the electrolyte. The olivine $LiFePO_4$ (LFP) is a polyanionic compound. These anions increase the cathode potential and stabilize the structure. In LFP, phosphorus occupies the tetrahedral sites while Li^+ and Fe^{2+} ions occupy the octahedral sites. Olivine has higher thermal stability.[1]

The spinel (example: $Li\ Ni_{0.5}Mn_{1.5}O_4$) (LNMO) cathodes are promising cathode material for LIBs as they are capable of delivering higher energy density due to their high operating voltage (~5 V vs Li/Li^+). Apart from this, spinel materials are environmental friendly and are of low cost. Although these cathodes have all the advantages they suffer from capacity fade during cycling due to the high operating voltage.[7-8] The spinel cathodes are unstable with carbonate based electrolyte. Electrolyte reduces at the electrode surface and also metal ions in cathode dissolve and travel through the electrolyte to the anode. This makes SEI unstable on the anode surface. But this issue can be resolved by the addition of electrolyte additives.[9]

Anode

The negative electrode of the Li-ion battery and is the host structure to accommodate Li^+ ion during the charging process. The common anode in use is graphite. The Li^+ ions intercalate into the graphene planes. (Figure 1.3a) The structure is mechanically stable and provide a good electrical conductivity. Due to the high availability of graphite the electrode is of lower cost. Importantly the volume changes during lithiation and delithiation is not significant (~10%).[10-11] The delithiation potential of graphite anode is also comparably low (~0.2 V vs. Li/Li^+). Although graphite anode is a promising anode material, it also has drawbacks. Electrolyte decomposition on the graphite surface can occur readily as graphite can act as a catalyst. As mentioned earlier when graphite is used with spinel cathodes dissolved Mn degrade graphite anode.[9]

Apart from graphite, $Li_4Ti_5O_{12}$ (LTO) is also a commercialized anode. (Figure 1.3b) Although it's expensive due to the cost of Ti it has a higher thermal stability and high cycle life. The volume changes during lithiation and delithiation is minimal (0.2%).[12] Due to the potential of LTO (1.55 Vs Li/Li^+) it can be operated at a potential above 1.00 V thus suppress the formation and growth of solid electrolyte interphase (SEI). The SEI formed during this process is also stable due to the low volume changes experience by LTO during charging and discharging.[12] The disadvantage with LTO is the gassing reaction with organic electrolytes at higher temperatures.

Another type of anode is alloying materials. Si is an example. Although it has extremely higher capacity the volume expansion during lithiation and delithiation is severe (270%). (Figure 1.3c) This undesirable volume expansion leads to the disruption of the SEI. Disruption of SEI means continuous reactions with electrolyte and increase in the cell impedance.[13]

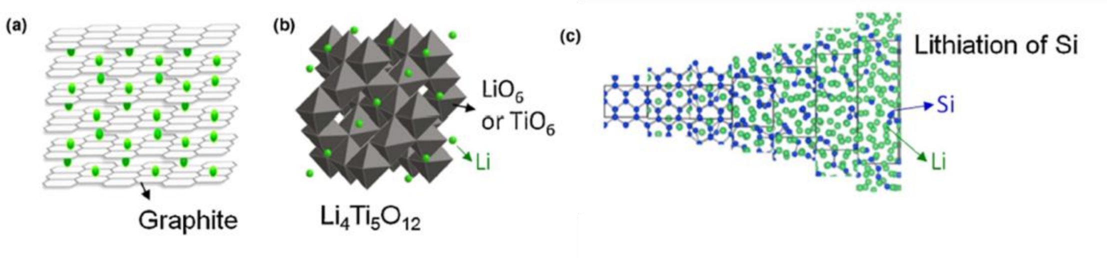

Figure 1.3: Schematic representation of (a) Graphite (b) LTO and (c) volume expansion of Si [1, 14]

Electrolyte

The electrolyte for Li-ion batteries usually consist of one or more lithium cation containing salts and organic solvents. The commonly used salt is $LiPF_6$. An ideal Li salt should be fully dissociated in organic solvent and should have a wide electrochemical window. Although $LiPF_6$ is chemically and thermally unstable it meets other necessary requirements to be considered as a successful lithium salt. The solvent for LIB also needs to meet several criteria. The lithium salt should be completely dissolved in the solvent, should be low viscous to facilitate the ion transport, should be inert to cathode anode and the cell components during the cell operation. Currently there's no single organic solvent that fulfill all these requirements. Thus, it's usually a combination of two or more solvents. The high dielectric constant of ethylene carbonate (EC) makes it a suitable candidate as the electrolyte. The limitation of EC is the high viscosity which limit the lithium ion transportation. This issue is resolved by mixing it with a low viscous linear carbonate such as ethylmethyl carbonate (EMC). The linear carbonates alone cannot operate above 4.0 V vs Li^+ as it oxidizes at the cathode surface. But mixture of EC and linear carbonates shows a stability on spinel cathodes until it reaches to 5.0 V vs Li^+.[5, 15]

Additives

Additives usually improve the performance of the batteries. In most cases these are sacrificial chemical compounds which form interphases to protect the electrodes or to reduce the electrolyte decomposition. When the compound introduced into the electrolyte is less than 10% of the total it can be considered as an additive. [15] Lithium bis(oxalato)borate (LiBOB) is an ionic additive. The importance of LiBOB is that it has a higher reduction potential of 1.7 V vs Li/Li^+ which is allows it to reduce at the graphite anode surface and form a stable interphase on the electrode protecting the electrode and suppressing the electrolyte degradation on the electrode surface.[15] BOB^- anion induce the formation of a stable SEI. The stability is enhanced by EC in the electrolyte.[16] Figure 1.4 represent the decomposition of LIBOB into semi carbonates. However, LiBOB increase the impedance of the cell. [9]

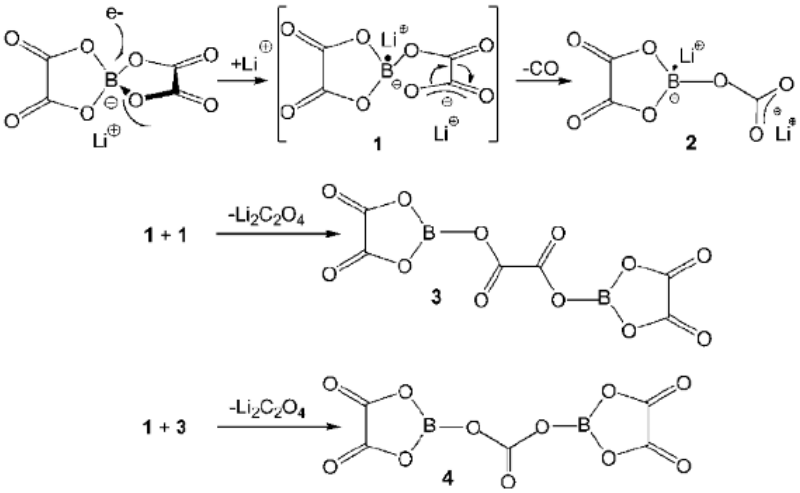

Figure 1.4: Semicarbonate formation of LiBOB [9]

CHAPTER 2

INCREASED CYCLING PERFORMANCE OF LI-ION BATTERIES BY PHOSPHORIC ACID MODIFIED $LiNi_{0.5}Mn_{1.5}O_4$ CATHODES IN THE PRESENCE OF LIBOB

by

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Introduction

Lithium ion batteries (LIB) are of high demand due to their wide range of applications including power source for portable consumer electronic devices, electric vehicle (EV) and hybrid electric vehicles (HEV).[6, 17] The applicability of LIB in EV and HEV is mainly due to the higher energy density they can deliver. One of the method to achieve higher energy density is by operating the battery at a higher voltage.[18] The use of high voltage cathode material in LIB construction is of interest. High voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$) is one of the commonly used high voltage cathode material in LIBs. $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) typically operates at 4.8 V vs Li/Li^+ and has a theoretical capacity of 147 mAh/g.[7, 19-21] The major issue of using this high voltage spinel is the electrolyte decomposition and metal ion dissolution during the cycling process due to the higher voltage used. For an example, the most common electrolyte $LiPF_6$ in organic solvents is found to be unstable at higher voltages and tend to decompose at LNMO electrode surface. The continuous reactions of electrolyte with the electrode during charging discharging processes lead to capacity fade of the lithium ion batteries.[7-8]

Several different methods have been used to control the electrolyte decomposition and metal ion dissolution during the cycling of high voltage LIBs. Surface coating with atomic layer deposition, use of different electrolyte formulations and incorporation of additives to the electrolyte are some examples. The atomic layer deposition (ALD) of Al_2O_3 considered to be a promising method.[22] However, the commercialization of ALD is not practical for large scale.

Incorporation of an additive which sacrificially undergo reduction during the first formation cycle forms a stable surface film which can control the electrolyte decomposition.[23-24] Lithium bis(oxalate)borate (LiBOB) identified as a good sacrificial additive. LiBOB in the electrolyte reduces at the electrode surface and form different semicarbonates to form a stable surface film that protects further electrolyte decomposition.[15-16]

In this study we have investigated the effect of inorganic modification (phosphoric acid modification) of LNMO cathode material and the use of 1% LiBOB in the electrolyte as an additive on LNMO/graphite full cells. The modification and the addition of LiBOB significantly improved the cycling performance of the full cells. Surface analysis methods were used to investigate the synergetic effect that contribute to enhance the cycling performance.

Experimental

Battery grade EC, EMC, lithium hexafluorophosphate ($LiPF_6$), dimethyl carbonate (DMC) and LiBOB were provided from BASF, Germany and they were used as received. Nitric acid was purchased from Sigma-Aldrich. Coin cell parts, celgard and glass fiber separators were purchased from MTI Corp. Phosphoric acid modified and unmodified $LiNi_{0.5}Mn_{1.5}O_4$ electrodes containing 85% (wt.) active material, 10% (wt.) conductive carbon (super C45) and 5% (wt.) binder were provided by Helmholtz Institute Ulm, Germany. Graphite anodes were prepared in the lab with 90% (wt.) graphite, 5% (wt.) conductive carbon (Super C65 and SFG6) and 5% (wt.) binder. The thickness of anodes was controlled to balance LNMO and graphite electrodes with a n/p ratio of 1.1-1.3.

LNMO/graphite coin cells for electrochemical performance studies were assembled in an argon filled glove-box in duplicates with trilayer polypropylene/polyethylene (PP/PE/PP) separator (Celgard) and a glass fiber. 100 µL of 1.0 M $LiPF_6$ EC/EMC (3/7, w/w) with and without 1% LiBOB was used as the electrolyte. Assembled cells were cycled at room temperature as follows between 3.5 V and 4.8 V; C/20 first cycle; C/10 second and third cycle; C/5 for remaining cycles for a total of 56 cycles.

Princeton Instruments (V3) was used to perform electrochemical impedance spectroscopy (EIS) on the coin cells after formation cycle and 56 cycles. The perturbation is 1 mV with the frequency range from 300 kHz to 10 mHz.

The cathodes and anodes of the cycled cells were harvested in an argon filled glove box. Cells were disassembled and washed with anhydrous DMC three times to remove residual electrolyte followed by vacuum drying at room temperature overnight. The electrodes were transferred to the X-ray photoelectron spectroscopy (XPS) chamber with a minimal exposure to air. PHI 5500 system with Al Ka radiation (hν = 1486.6 eV) under ultrahigh vacuum conditions was used for the measurements. The final adjustments were done referring to C-C of C1s at 284.5 eV. Fourier transformed infrared (FTIR) spectra for discharged electrodes were obtained on Bruker Tensor 27 with Attenuated Total Reflectance (ATR) accessory with Germanium crystal, 512 scans with the resolution of 4 cm^{-1}.

For analysis of cycled anodes with inductively coupled plasma-mass spectroscopy (ICP-MS), copper foils of anodes rinsed with DCM to remove any residual electrolytes were removed. 2% HNO_3 was added to dissolve the residual solids and then diluted to 10.00 mL. Solutions were sonicated, left for digestion, filtered and carried out ICP-MS analysis with necessary dilutions.

Results and Discussion

Cycling data of LNMO/Graphite full cells

Figure 2.1 (a) shows cycling performance of phosphoric acid modified and unmodified LNMO/graphite cells cycled with standard electrolyte and electrolyte with added LiBOB (1 wt.%) at 25 ^{0}C. Figure 2.1 (b) displays the coulombic efficiencies (CE). From the first discharge capacity there is a huge improvement in the cells with phosphoric acid modified electrodes. The first discharge capacity for unmodified LNMO with standard electrolyte is 81.6 mAh/g while modified cell with standard electrolyte delivers a capacity of 110.0 mAh/g. Unmodified cells cycled with standard electrolyte has a first CE of 47.3% whereas modified cells with standard electrolyte shows a first CE of 68.6%. The addition of LiBOB to both the cells display improvement in discharging capacities. LiBOB increase the discharging capacity of unmodified cells to 104.3 mAh/g and in phosphoric acid modified cells to 120.1 mAh/g. In addition, the cells with added LiBOB displays better CEs compared to standard electrolyte Figure 2.1 (b).

Electrochmical Impedance Spectra(EIS)

The EIS of phosphoric acid modified and unmodified LNMO/graphite full cells with and without LiBOB in the electrolyte after the first formation cycle (a) and after 56 cycles (b) are shown in figure 2.2. The EIS spectra shows that after the formation cycle the impedance of the batteries with LiBOB is lower compared to the batteries with standard electrolyte (Figure 2.2 (a)). However, after all 56 cycles this reverse and the impedance of batteries with LiBOB is higher compared to the standard (Figure 2.2 (b)). As LiBOB decomposes on the electrode surface the surface film on the electrode gets much thicker.[9, 25-26] The increase in impedance of batteries with LiBOB during the cycling can be attributed to the thicker surface layer. The impedance of the batteries with phosphoric acid modified LNMO display a lower impedance compared to unmodified LNMO. This explains the higher discharge capacities observed for the cells with phosphoric acid modified LNMO cathodes.

Surface analysis of anodes and cathodes

Attenuated total reflectance- Fourier transformed infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra of fresh and cycled anodes (a) and cathodes(b) are shown in figure 2.3. FTIR was carried out to investigate the composition of the surface layers formed on the electrode surfaces. Anode of the batteries cycled with the standard electrolyte contains IR peaks consistent with the presence of $ROCO_2Li$ at 1611 cm^{-1} and Li_2CO_3 at 1431 cm^{-1}. [27-28] The batteries with LiBOB additive do not show any evidence for the presence of these two peaks. This suggest that in the presence of LiBOB, the surface film has a different chemical composition. Further, the peak at 1740 cm^{-1} is characteristic of poly(ethylene carbonate). This peak is observed on cycled anodes and cathodes with standard electrolyte and also on unmodified cathode surface even in the presence of LiBOB. This suggest that LiBOB diminish the formation of poly(ethylene carbonate) on anode surface.[19] However this is true only if cathode is modified with phosphoric acid. The FTIR spectra of anodes with LiBOB and modified cathode with LiBOB completely overlap with each other. This suggest that the surface film formed on above mentioned surfaces are similar. The peak at 1773 cm^{-1} could be residual EC from the electrolyte.[28]

X-ray photoelectron spectroscopy

XPS spectra of anodes obtained from cycled batteries (Figure 2.4) provide additional information on the composition of the surface films formed on electrodes in the presence and absence of LIBOB and also the effect of phosphoric acid modification. F1s spectra for anodes indicate LiF peak is getting weaker for phosphoric acid modified batteries and the intensity further reduces with the addition of LiBOB to the electrolyte. This is consistent with suppressed $LiPF_6$ reduction by modified electrodes as well as LiBOB. In C1s the peaks at 286.8 eV and 290.3 eV on the cycled anodes corresponding to C-O and CO_3 indicate the new products formed during the cycling. The intensities of the peak at 290.3 eV in C1s and C-O peak at 533.0 eV in O1s is higher when LiBOB is present in the electrolyte.[29-30] This is an evidence for the passivation layer formed in the presence of LiBOB.

XPS element spectra of cathodes are provided in figure 2.5. P2p spectra of fresh electrodes show the presence of phosphors in modified electrode (134.0 eV). In C1s spectra C-C peak intensities of cycled electrodes are much lower compared to the fresh electrodes. This indicates the presence of a surface film on the cycled electrodes. The peak at 688.0 eV in F1s indicates $Li_xPF_yO_z$ (the binder for LNMO is not PVDF) in the surface film. The lower impedance of the cells with standard electrolyte is a result of increased $Li_xPF_yO_z$. The intensity of the peak is reduced in the presence of LiBOB. This is attributed to reduced $LiPF_6$ decomposition in the presence of LiBOB. The intensity of metal oxide peak at 529.5 eV in O1s is reduced with the cycling. Intensity is higher for the fresh electrodes. This indicates the formation of a surface film during cycling.

XPS data suggests that phosphoric acid modification suppress the decomposition of electrolyte on the surface of the electrodes.

Inductively coupled plasma-mass spectroscopy (ICP-MS)

The most common issue with LNMO is the metal ion dissolution during cycling. To quantify the metal ion deposition in the anodes of cycled cells, ICP-MS was carried out. ICP-MS data for anodes harvested from the LNMO/graphite full cells are shown in figure 2.6. The Mn and Ni concentration for the cells with unmodified LNMO with standard electrolyte are found to be 5642 ppb and 2746 ppb respectively. This is the highest concentrations observed for all four types of cells. Which suggest metal ion dissolution is higher for unmodified electrodes and standard electrolyte. Addition of LiBOB to the same setup suppress the metal ion dissolution by ~10 folds (Mn 454 ppb and Ni 383 ppb). Mn and Ni concentrations for anodes from the cells with modified electrodes are 539 ppb and 198 ppb respectively. Which is a significantly reduced amount compared to unmodified LNMO cells with standard electrolyte. Finally, phosphoric acid modified batteries in the presence of LiBOB shows the highest reduction in metal ion dissolution (Mn 170 ppb and Ni 46 ppb). This trend in reduction of metal ion dissolution is in agreement with the trend in discharging capacities of LNMO/graphite full cells. The reduction of metal ion dissolution contributes to the increased cycling performance.

Conclusion

The cycling performance of phosphoric acid modified and unmodified LNMO/graphite full cells with standard electrolyte with and without LiBOB has been investigated. The cycled cells from the beginning exhibited enhanced performance by the phosphoric acid modification as well as the addition of LiBOB. The cells with LiBOB also displayed a better coulombic efficiency.

Ex-situ surface analysis of harvested cathodes and anodes have been carried out through FTIR, XPS and ICP-MS. FTIR indicated that the surface film formed in the presence of LiBOB is similar on anodes and when LNMO is modified with phosphoric the surface film formed on cathode in the presence of LiBOB is similar to anode film. The surface film formed in the presence of LiBOB suppresses the dissociation of $LiPF_6$ and electrolyte decomposition. Phosphoric acid modification of LNMO electrodes drastically reduce the metal ion dissolution into the electrolyte during the cycling and the surface film form by the reduction of LiBOB further suppress the metal ion dissolution.

The increased cycling performance of LNMO/graphite full cells can be attributed to the reduced metal ion dissolution to the electrolyte and deposition on anode due to phosphoric acid modification of the cathode and presence of LiBOB in the electrolyte.

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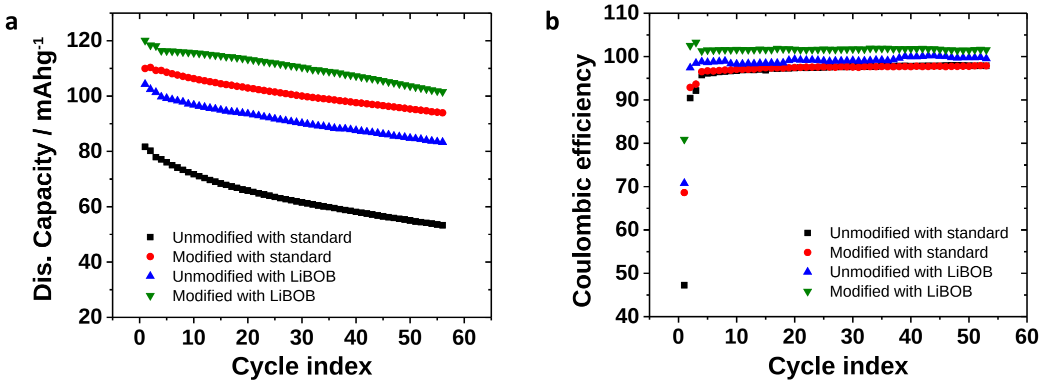

Figure 2.1: Cycling performance (a) and coulombic efficiency of Phosphoric acid modified and unmodified LNMO/graphite full cells with and without LiBOB in 1.0M $LiPF_6$ EC/EMC 3/7 (w/w)

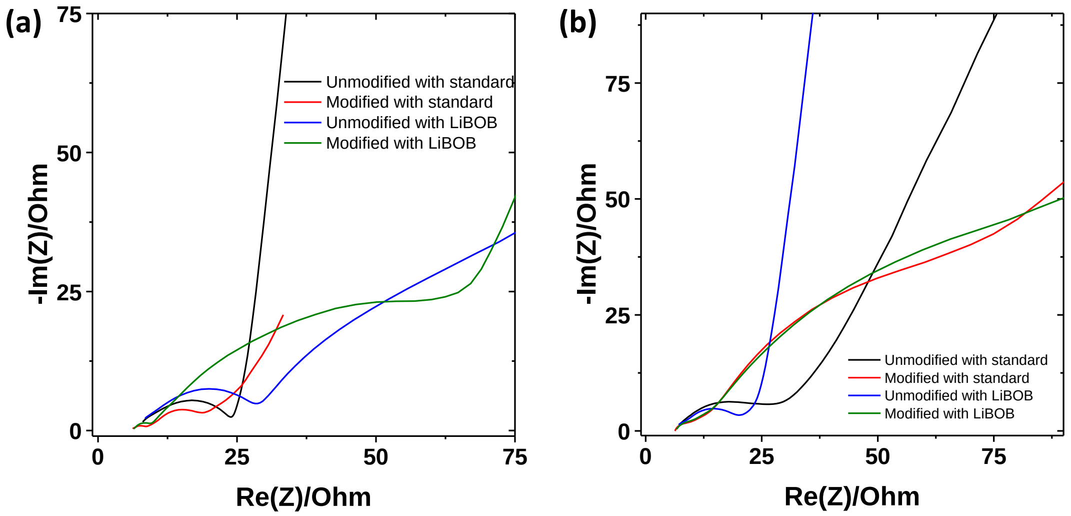

Figure 2.2: EIS measurements of phosphoric acid modified and unmodified LNMO/graphite full cells with and without LiBOB after the formation cycle (a) after 56 cycles (b)

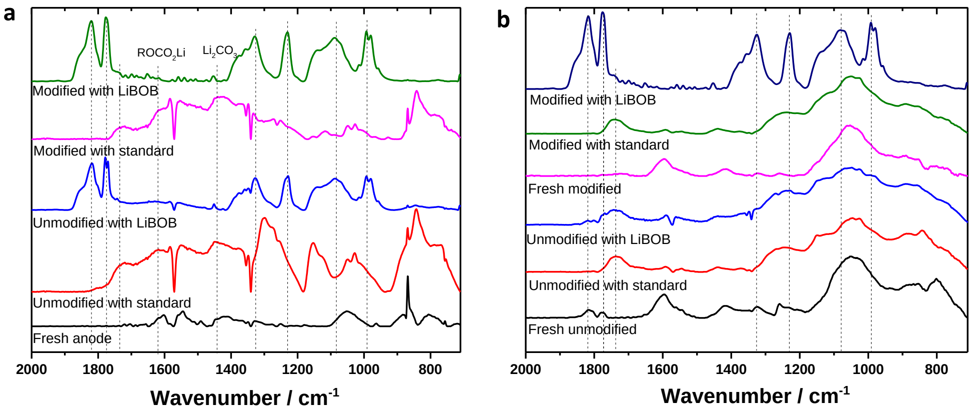

Figure 2.3: ATR-FTIR surface analysis of fresh and harvested graphite (a) and LNMO (b) after cycling

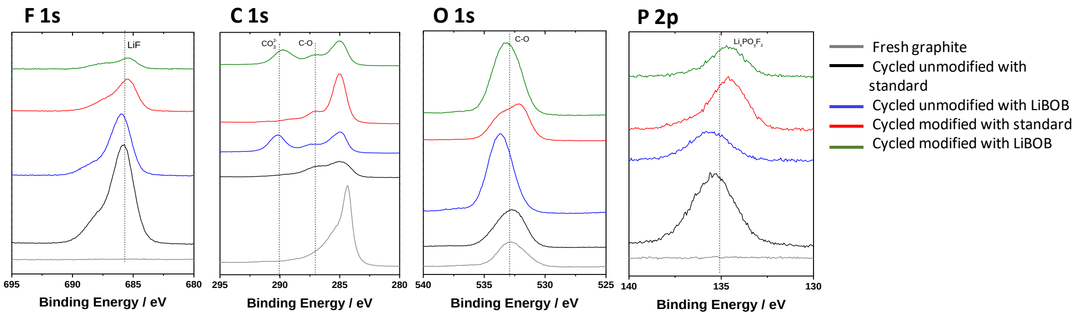

Figure 2.4: XPS surface analysis of fresh and cycled graphite in phosphoric acid modified and unmodified LNMO/graphite full cells with and without LiBOB in the electrolyte

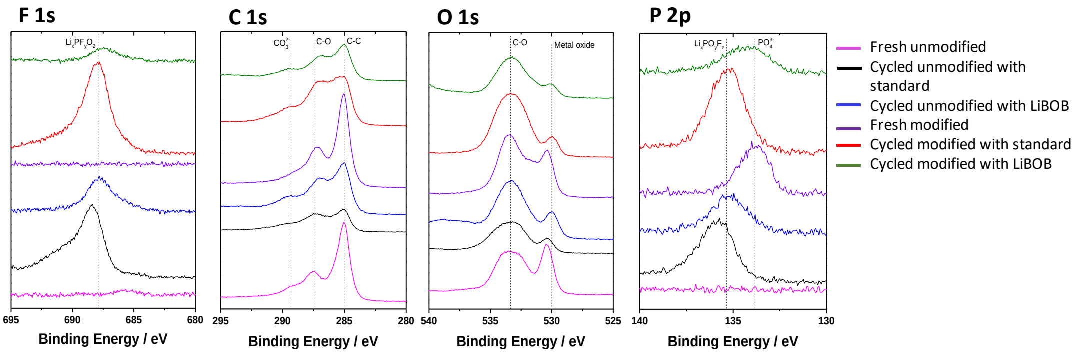

Figure 2.5: XPS surface analysis of fresh and cycled LNMO in phosphoric acid modified and unmodified LNMO/graphite full cells with and without LiBOB in the electrolyte

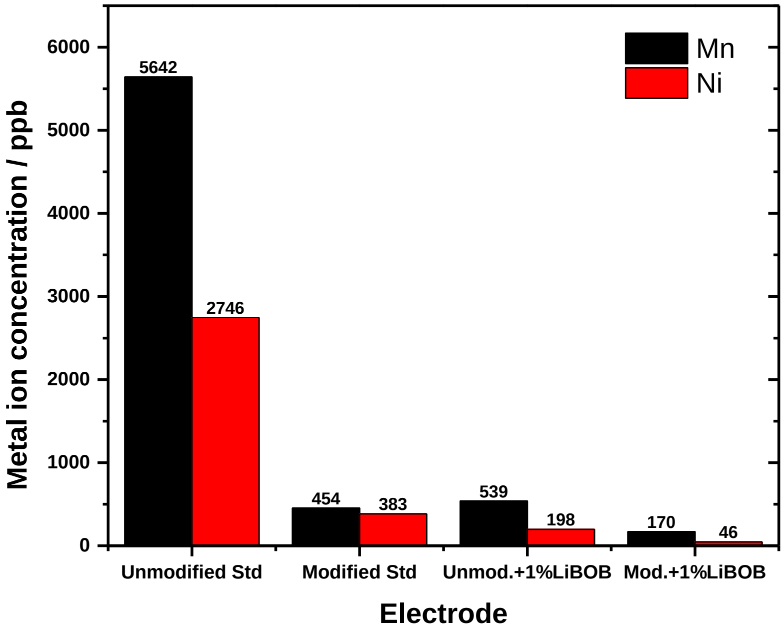

Figure 2.6: Mn and Ni concentrations on the harvested anodes analyzed by ICP-MS