

IMPROVEMENT OF THERMAL STABILITY OF LI-ION BATTERIES BY POLYMER COATING OF LiMn_2O_4

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INDEPENDENT ASSESSMENT REPORT (IAR)

**IMPROVEMENT OF THERMAL STABILITY OF LI-ION BATTERIES BY
POLYMER COATING OF LiMn_2O_4**

EISG AWARDEE

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PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace. The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2.4 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

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PIER funding efforts are focused on the following six RD&D program areas:

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- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Energy Systems Integration

The EISG Program Administrator is required by contract to generate and deliver to the Commission an Independent Assessment Report (IAR) on all completed grant projects. The purpose of the IAR is to provide a concise summary and independent assessment of the grant project in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions. The IAR is organized into the following sections:

- Introduction
- Objectives
- Outcomes (relative to objectives)
- Conclusions
- Recommendations
- Benefits to California
- Overall Technology Assessment
- Appendices
 - Appendix A: Final Report (under separate cover)
 - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the IAR, please visit the EISG program page on the Commission's Web site at:

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For more information on the overall PIER Program, please visit the Commission's Web site at <http://www.energy.ca.gov/research/index.html>.

Improvement of Thermal Stability of Li-ion Batteries by Polymer Coating of LiMn₂O₄

EISG Grant # 01-21

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Introduction

Rechargeable batteries are widely used as energy storage systems for renewable-energy technologies and power-quality systems. A battery system can give renewable-energy technologies around-the-clock viability by storing the electrical energy they produce for its most economical, strategic, and efficient uses. Batteries that combine high energy density with low cost and that are environmentally friendly would benefit the California renewable-energy market. Lithium-ion (LiCoO₂) battery technology offers higher energy density than most other commercial types, but at a generally higher cost per cycle. Lithium cobaltate batteries have been in commercial use since 1991. A new lithium-ion battery with different cathode chemistry (LiMn₂O₄) has been identified as a possible replacement. It contains manganese (spinel) instead of cobalt and would be inherently safer and cheaper to produce. However, the spinel cathode has problems with capacity fading during cycling and with storage at elevated temperatures (55°–66° C). Specifically, capacity fading occurs during cycling because the crystal geometry weakens, especially in the cathode-surface region. At elevated temperatures dissolution of the LiMn₂O₄ into the electrolyte enhances this process and leads to irreversible battery deterioration.

Resolution of issues relating to capacity fading would permit the manufacture of a high-performance battery at lower cost. The raw-material price of manganese oxide is \$2.29/kg, while cobalt oxide runs \$39.60 to \$41.80/kg. Lithium cobaltate batteries also incur the extra cost of a thermal protection circuit necessary to ensure safety during operation. Spinel is inherently safer, more environmentally benign, and less toxic than lithium cobaltate.

The principal investigator predicted that the use of surface-modified LiMn₂O₄ (SM-LMO) as the cathode material would alleviate or resolve the problems of capacity fading during cycling and after storage at elevated temperatures (55°–66° C). The researcher proposed to minimize surface degradation by surface modification on the molecular level. Specifically, the project used polymer-coated particles of LiMn₂O₄ to fabricate an experimental cathode. The principal investigator hypothesized that the polymer coating would inhibit Mn⁺ dissolution at the surface and improve thermal stability at elevated temperatures, thereby extending battery life.

Objectives

The goal of this project was to determine the feasibility of using surface-modified LiMn₂O₄ (SM-LMO) as the cathode material to reduce capacity fading in a rechargeable lithium-ion battery by inhibiting Mn⁺ dissolution at the surface and improving thermal stability at elevated temperatures (55°–66° C). The researcher established the following project objectives:

1. Finalize the methodology for two surface treatments of the LMO cathodes.

- Determine the surface chemistry for each surface-modified LMO cathode.
- Demonstrate that Mn^+ dissolution can be reduced by 30% to 50% in LMO cathodes.
- Demonstrate that capacity fading can be reduced by 30% to 50% in LMO cathodes.
- Show from the research findings that a successful surface treatment can reduce the manufacturing cost of lithium-ion batteries by 10% to 20%.
- Investigate the effect of surface modifications on the reactions at the cathode/electrolyte interface and on the mechanism of capacity fading.

Outcomes

- Two methods of cathode coating were implemented: one way consisted in applying PDDA¹ on the LiMn_2O_4 pellet; the other way consisted in applying a thin, molecular film on the LiMn_2O_4 powder before cathode fabrication. The investigation was limited to a PDDA solution-concentration range of 10 to 100 mM² because the measured storage capacity for larger concentrations is lower than the untreated cathode. PDDA solution concentrations of 10, 20, 30, 50, and 100 mM were applied to the cathode pellet (weighing 8 mg) and powder (weighing 0.2 mg). For each of the PDDA concentrations investigated, more PDDA absorbed to the powder than the pellet.
- Transmission electron microscopy (TEM) confirmed the existence of the polymer coating on the cathode surface. Scanning electron microscopy (SEM) showed that more PDDA absorbed on small LiMn_2O_4 particles than larger ones because the smaller ones have a larger relative surface area. Results indicate that capacity does not depend strongly on the thickness of the polymer layer.
- The researcher did not quantify the reduction in Mn^+ dissolution.
- Capacity stabilities of the PDDA-coated pellet and powder are $4.3 \pm 1.1\%$ and $9.3 \pm 5.3\%$, respectively, after 5-10 charge/discharge cycles at room temperature. On average, the charge/discharge curves of the untreated PDDA-coated cathode after storage at 70°C for one week showed 18% to 20% loss of initial capacity. Diminished capacity after storage was about 12% and 6% for the PDDA-coated pellet and powder, respectively.
- The findings do not specifically demonstrate that surface modification can reduce the manufacturing cost of lithium ion batteries 10%-20%. However, the researcher did note the wide difference in price of raw materials—manganese oxide (\$2.29/kg) versus cobalt oxide (\$39.60/kg to \$41.80/kg). Additionally, PDDA can be used as a binder to reduce the amount of Teflon used in fabricating the cathode. That may further reduce cathode-manufacturing costs.
- Cathode surface reactions were observed using *in situ* electrochemical atomic force microscopy (EC-AFM) at room and elevated temperatures. The measured capacity fading after storage decreased for coated cathode pellet and LiMn_2O_4 powder. Capacity fading measured on cathodes made of PDDA-coated LiMn_2O_4 was very small for cathodes obtained from powder coated in solution containing 30 and 50 mM PDDA.

¹ poly diallyldimethylammonium chloride

² millimolar

Conclusions

The researcher in this project provided a new approach to extending lithium-ion battery life. The data, while promising, are not sufficient to prove the feasibility of the concept.

1. Coating with a polymer film successfully modified LiMn_2O_4 nanoparticles used as active material in cathode fabrication. The coating method is sensitive to the initial powder dispersion and mixing procedure.
2. TEM, SEM and Energy Dispersive X-ray Analysis (EDAX) confirmed the formation of a thin polymer film on the surface of the LiMn_2O_4 nanoparticles. The Technical Reviewer indicated that the proposed model may be wrong because the results should have shown a strong relationship between cathode capacity and the thickness of the polymer layer.
3. The researcher did not specifically quantify the 30% to 50% reduction in LMO cathode Mn^+ dissolution; however, the researcher hypothesizes that the polymer coating protects the LiMn_2O_4 particle surface from the full contact with the electrolyte and possibly blocks surface reactions that are responsible for capacity fading.
4. The researcher did not meet his initial goal of reducing capacity fading by 30% to 50% in LMO cathodes. However, there was measurable improvement in capacity fading—approximately 6% to 14% with the SM-LMO cathode after storage at room temperature. The researcher hypothesized that the higher capacity loss for the coated powder might be the difference in its mixing properties. It would have been beneficial if measured charge/discharge cycling results (5-10 cycles) for the untreated cathode had been included in the report. Without this data it is hard to draw a comparison with the measured results for the treated cathode.
5. The researcher's claim of reduced manufacturing costs was based solely on the lower raw-material price for manganese oxide compared to cobalt oxide. The true manufacturing costs are difficult to substantiate at this point in the development process.
6. The *in situ* AFM observation of the cathodes at room temperature shows changes in surface topography that follow potential cycling. These are attributed to the lithiation/delithiation processes that accompany the change in potential during charge-discharge cycling. These changes are related to either Mn^+ dissolution or film formation on the cathode surface. The researcher hypothesizes that the possible degradation mechanism is the reversible dissociation of the electrolyte salt LiPF_6 to LiF and PF_5 . The PF_5 can, in turn, react with the manganese oxides on the surface to form manganese difluoride on the cathode and soluble products in the electrolyte. The soluble products in electrolyte could be POF_3 and PO_2F_2 .

Recommendations

Further optimization of the polymer coating and more detailed characterization of the mechanism of capacity fading in LiMn_2O_4 cathodes during cycling and storage at elevated temperatures are needed. The researcher should consider the following recommendations upon commencement of additional work in this area:

1. Reinvestigate the relationship between the capacity and thickness of the polymer layer. Perhaps there should be a stronger relationship.

2. Refine the cathode coating method, specifically, initial powder dispersion and mixing procedure.
3. Determine the optimal amount of PDDA that will yield maximum stability of the modified cathode.
4. Draw a comparison of charge/discharge cycling results (after multiple cycles) for the untreated cathode versus the treated cathode. Investigate other performance parameters, e.g., charge/discharge rate, diffusion constant, etc.
5. Investigate further the mechanism of capacity fading during cycling and storage at elevated temperatures. Establish the nature of the cathode surface film formed following the potential cycle.
6. Develop new image-processing techniques for studying the local changes in cathode-surface topography.
7. Quantify reductions in manufacturing costs for spinel lithium-ion batteries as a result of using surface-modified LiMn_2O_4 cathodes.

Benefits to California

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The employment of a lower-cost, high-performance battery in the California market will enable renewable-power systems and energy storage systems to more effectively reduce peak demand on the electric grid, directly benefiting ratepayers. Potential energy and cost savings to ratepayers would result from reducing transmission losses in electricity delivery and extending both the service life of grid-system equipment and the time period between grid-system upgrades. In addition, environmental impacts of the California electricity supply and transmission and distribution system would be reduced. Since the technology is still far from commercialization, it is difficult to estimate the rate at which these benefits would accrue to California ratepayers.

Overall Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researcher's overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

This project is an attempt to develop high-energy-density rechargeable batteries that also are fast, inexpensive, and environmentally friendly. Energy storage systems that offer high-energy density are essential for commercial, stationary power systems (renewable and emergency power) and for power-quality systems. The researcher will prepare a white paper documenting project results and distribute it to battery manufacturers. Additionally, the researcher has established contacts with BP Solar in Fairfield, CA and with Mitsubishi Chemical in Mountain View, CA.

Engineering/Technical

This project successfully synthesized a polymer-coated LiMn_2O_4 cathode. In addition, the following tasks were accomplished:

- Conducted capacity measurements of lithium-ion batteries over cycles and elevated temperatures and identified degradation of performance.
- Identified polyion PDDA as the first candidate for surface coating.
- Modified LiMn_2O_4 nanoparticles by coating with PDDA polymer film.
- Confirmed polymer coating by TEM, SEM, and EDAX analyses, which support the formation of a thin polymer film on the cathode surface.
- Demonstrated improved capacity fading with coated cathode after storage at elevated temperatures.

Legal/Contractual

The researcher is considering applying for a patent. The report is under consideration for publication by the American Chemistry Society (ACS).

Environmental, Safety, Risk Assessments/ Quality Plans

Formal quality planning for this project at such an early stage of research would be premature. Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental.

Production Readiness/Commercialization

This project is in the early stage of research and not yet ready for commercialization.

Appendix A: Research Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted).

**ENERGY INNOVATIONS SMALL GRANT
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EISG FINAL REPORT

**Improvement of Thermal Stability of Li-ion Batteries
by Polymer Coating of LiMn_2O_4**

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Abstract

A new approach has been used to minimize surface degradation of the LiMn_2O_4 cathode in lithium ion batteries by using surface modification. Since one of the main reasons for capacity fading in Li-ion batteries is Mn dissolution from the surface, we performed research to halt the dissolution of manganese into the electrolyte solution using polymer coatings modification on molecular scale. We characterized the new material by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), and performed a detailed study of the new cathode material under potential and temperature control in organic electrolyte using electrochemical techniques and *in situ* Electrochemical Atomic Force Microscopy (EC-AFM). The main objective was to investigate the effect of surface reaction at cathode/electrolyte interface on the mechanism of capacity fading using *in situ* EC-AFM.

We have successfully coated the LiMn_2O_4 particles with a polymer layer and obtained improved electrochemical stability of the cathode in organic electrolyte at room and elevated temperature. Our hypothesis is that the polymer layer blocks surface reactions that cause degradation. The method for surface modified LiMn_2O_4 (SM-LMO) particles extends the lifetime of the battery by arresting the Mn^+ dissolution, thereby increasing the battery stability. The process of polymer adsorption is simple and cheap and economically viable.

Key Words: Lithium Battery, Cathode, LiMn_2O_4 , Polymer Film, Electrochemical Atomic Force Microscopy, Scanning Electron Microscopy.

Executive Summary

1. Introduction

This project is a successful attempt to develop high energy density, fast, inexpensive and environmentally friendly novel rechargeable batteries. The spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ is a promising cathode material for rechargeable lithium ion batteries because of its high voltage, low cost, and safety. However, the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode has problems related to capacity fading during cycling and storage at elevated temperatures and these problems need to be solved before commercial usage. We succeeded in obtaining novel cathodes based on LiMn_2O_4 that show excellent stability at elevated temperature.

There is a challenge in the lithium-ion battery field to identifying the changes on the cathode surface and to determine the mechanisms of capacity fading at high temperatures. This report contains both the methodology to obtain surface modified active material for Li-ion batteries and characterization of the cathode material. Our aim was to enhance the performance of LMO based batteries by surface modification on a molecular scale. We present here several coating methods along with the electrochemical performance of the modified cathode. Investigation of SM-LMO cathode materials using various electrochemical and surface sensitive techniques has provided the information needed to understand the effect of the surface modification on the surface chemistry of the cathode in organic electrolyte.

Additionally, we present the development of a new strategy to study the effect of surface modification on the reactions at cathode/electrolyte interface, which are responsible for the capacity fading. The surface process was monitored by *in situ* electrochemical AFM under potential and temperature control using a new design for an electrochemical AFM cell. Direct observation of the surface under potential and temperature control provides a nanoscale understanding of the local redox reactions at cathode/electrolyte interface. The development of a high-resolution *in situ* EC-AFM method for battery studies at elevated temperature makes possible to speed up the process, to do predictive degradation studies and predict the battery properties. As an outcome of the EC-AFM image processing, we started to exploit the feature extraction capabilities of wavelets to enhance the information obtained from AFM images. We propose to develop further software tools that can be integrated with imaging equipment to provide users more insight towards understanding surface images.

2. Project Objectives

The overall objective of this project was to determine the feasibility of using lithium manganese oxide as a cathode material in rechargeable lithium ion batteries to achieve higher voltage, lower cost and increased safety.

Project objectives were to:

- Finalize the methodology for two surface treatments of the LMO cathodes.
- Determine the surface chemistry for each surface modified LMO cathode.
- Demonstrate that Mn dissolution can be reduced by 30-50 % in LMO cathodes.
- Demonstrate that capacity fading can be reduced by 30-50 % in LMO cathodes.
- Show from the research findings that a successful surface treatment can reduce the manufacturing cost of lithium ion batteries by 10-20 %.
- Investigate the effect of surface modifications on the reactions at cathode/electrolyte interface and on the mechanism of capacity fading.
- Surface characterization and statistical analysis, using wavelets.

Our approach to minimize surface degradation of LiMn_2O_4 by using surface modification on molecular scale has integrated several objectives and tasks as presented above. Besides concluding a reproducible procedure for surface treatments of the LMO cathodes, we studied the surface modification of the cathode by conducting detailed investigations of the electrochemical behavior and surface characterization by various surface structure sensitive techniques. In the following, the materials used in our experiments, sample preparation and characterization techniques are presented.

2. Project Outcomes

We used various methods for applying the coating in order to find which procedure results in increased characteristics of the batteries. One method consisted in applying a polymer film on a cathode pellet and the other method (with several manufacturing condition variables) consisted in applying a thin, molecular, film on the LiMn_2O_4 powder before cathode fabrication. The PDDA amount adsorbed on pellet and LiMn_2O_4 powder has been obtained using a UV-Visible Spectrophotometer (Varian Analytical Instruments, CA). The PDDA amount adsorbed on LiMn_2O_4 powder and on the pellet from solutions with various PDDA compositions has been determined.

The electrochemical behavior of the modified cathode was analyzed using various electrochemical techniques. Charge/discharge properties and cyclic voltammetry of the cathode were measured as well as the electrochemical properties of the cathode *before* and *after storage* at elevated temperature. The surface of the cathode was observed by atomic force microscopy (AFM, Nano Scope IIIA, Digital Instruments) using various imaging modes in air and in electrolyte. The electrochemical cell used in EC-AFM is similar to the cell used for other electrochemical measurements, e.g. it consists of cathode material as the working electrode and two lithium sheets as counter and reference electrodes. Active electrochemical and temperature control, and simultaneous observations of the surface reactions was carried out in the EC-AFM set-up. Energy Dispersive X-ray analysis, Scanning Electron Microscope (SEM) and Transmission Electron Microscopy has been performed in order to characterize the polymer coating.

4. Conclusions

The main conclusions of this study are:

- Coating with a polymer film successfully modified LiMn_2O_4 nanoparticles used as active material in cathode fabrication. The coating method is sensitive to the initial powder dispersion and mixing procedure.
- TEM, SEM and EDAX analyses have confirmed the polymer coating. These techniques support the formation of a thin polymer film on the surface of LiMn_2O_4 nanoparticles,
- Coating the cathode pellet or the LiMn_2O_4 powder results in an improved stability of the coated cathode during charge/discharge cycling in organic electrolyte at room temperature.
- The measured capacity fading after storage decreased for coated cathode pellet and LiMn_2O_4 powder. Capacity fading measured on cathodes made of PDDA-coated LiMn_2O_4 powder was very small for cathodes obtained from powder coated in solution containing 30 and 50 mM PDDA.

- The *in situ* AFM observation of the cathodes at room temperature shows changes in surface topography that follow the potential cycle. These are attributed to the lithiation/delithiation process that accompanies the change in potential during a charge-discharge cycle.
- Our hypothesis is that the polymer layer prevents surface reactions that cause degradation.

5. Recommendations

Further studies are needed to optimize the amount of the PDDA adsorbed on particles that yields maximum stability of the modified cathode. The observed changes in surface topography of the cathode are related to either Mn^{+} dissolution or film formation on the cathode surface but the nature of the film is not yet established. The actual mechanism of capacity fading needs also further investigations. Although the complex reactions that take place on the cathode surface have not been completely elucidated, the improvement in battery performance demonstrates that the coating method proposed in this research prevents degradation reactions occurring on the cathode surface.

We have begun a new project on the development of new image processing techniques for studying the local changes in surface topography using wavelet analysis of AFM images of surfaces.

6. Public Benefits to California

This project is a successful attempt to develop high energy density, fast, inexpensive and environmentally friendly novel rechargeable batteries. There is a number of energy, economic, and environmental benefits to California concerning the development of $LiMn_2O_4$ batteries used for energy storage and power quality systems. The main benefits include: reduction in pollution and reduction in manufacturing cost.

Introduction

The spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ is a promising cathode material for rechargeable lithium ion batteries because of its high voltage, low cost, and safety [1-3]. However, the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode has some problems related to the capacity fading during cycling and storage at elevated temperature [4] and these problems should be solved before commercial usage.

Studies conducted to clarify the mechanism of lithium battery deterioration [5-7] have revealed that capacity fading is caused by changes in the cathode potential itself and by an increase in the cathode resistance. These phenomena may occur through a combination of various processes at elevated temperatures, which include: 1) electrolyte decomposition at a voltage range higher than 4 V; 2) dissolution of $\text{Li}_x\text{Mn}_2\text{O}_4$ into the electrolyte through the disproportionation reaction of $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$; 3) irreversible structure transition due to Jahn-Teller distortion at the discharged state; 4) transformation of an unstable two-phase structure in the high voltage region to a more stable single-phase structure through loss of MnO [8, 9]. Jang et al. [10] also reported that Mn dissolution in the cathode causes capacity fading by two different pathways. The first pathway is a material loss of the loaded spinel and the second pathway is a polarization loss due to cell resistance increase. Specifically, the resistance increase is due to a high contact resistance at the spinel/carbon interface caused by Mn dissolution. The main cause of the contact resistance is the formation of a film on the surface of the cathode, which reduces Li^+ ions from transferring in and out of the cathode. In this context, investigations on the surface processes including intercalation/deintercalation of Li^+ ions have been widely conducted on anode material [11-13] but only a limited number of studies have been performed on the cathode surface. Blyr et al. [4] obtained scanning electron microscope (SEM) micrographs of $\text{Li}_x\text{Mn}_2\text{O}_4$ cathodes left at 55°C for two months and observed a pitted surface due to Mn dissolution. Antonini et al. [14] studied with SEM a Ga-doped spinel cathode surface after storage at 55°C and concluded that a surface layer is formed during storage at open circuit following the first charge.

Cathode deterioration appears to be due to surface rearrangements of species during charge/storage/ discharge process. The development of surface structure-sensitive techniques in recent years has led to *in situ* electrochemical atomic force microscopy (EC-AFM), which has opened the door for efficient and detailed study of the correlation among surface chemistry, morphology, 3D structures, electrochemical response and performances of electrodes. EC-AFM studies on Li-ion battery electrodes will give useful information that is necessary to understand the surface processes on the cathode. This information can also be related to measurements from other surface-sensitive techniques.

In the past few years, AFM studies have been focused on lithium or graphite anode materials. The relevance of using AFM and EC-AFM in surface reaction studies on the anode in secondary batteries is found from the research work done on Li [15,16], and from the graphite surface during Li intercalation/deintercalation process [17-21]. Several reviews [22-24] emphasize the importance of *in situ* AFM studies of surface phenomena along with other *in situ* and *ex situ* surface sensitive techniques such as FTIR spectroscopy, electrochemical quartz crystal microbalance (EQCM) and impedance spectroscopy (EIS).

The surface chemistry and morphology of the anode in organic solutions was extensively studied and is better understood than the cathode. Generally, the scanning probe microscopes (SPM) such as AFM and STM were mainly used in air to characterize the new cathode materials obtained by different methods (i.e. sol-gel, spin coating, pulse laser deposition) [25-28].

Although the spinel LiMn_2O_4 oxide for rechargeable Li ion batteries has been intensively studied by electrochemical methods, there is no systematic study by AFM or EC-AFM on the cathode surface although the AFM is an effective tool for imaging the surface of the actual composite electrode at micro and nano scale level in organic electrolytes.

Therefore, there is a challenge in the lithium-ion battery field to identifying the changes on the cathode surface and to determine the mechanisms of capacity fading at high temperatures. In our previous work, besides other surface sensitive techniques (e.g. EDAX, XPS), we used AFM in air at room temperature. There are several imaging modes that can be used for imaging cathode material surface such as contact AFM for topographic imaging, tapping mode AFM (TM-AFM) that operates by vibrating the cantilever near its resonance frequency, and lateral force (LFM) that images the frictional differences in a sample by detecting the lateral bending of the cantilever as a result of frictional properties. We used these imaging techniques to provide a basis for composite electrode imaging that is important in determining the imaging mode that maximize the information on surface topography and binder distribution. Our previous AFM observations performed in air on the surface of the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode before and after storage at 70°C suggest that a film deposition on the cathode surface is responsible for the decrease of Li^+ ion transport conductivity into and out of the cathode [29]. However, even though morphology changes were clearly observed, no change in the roughness of the surface could be detected. We have also used the electrochemical AFM at room temperature because, if a surface reaction is involved in capacity fading, the EC-AFM technique can provide additional useful information about the mechanism of capacity fading. The results have demonstrated a complex deposition/dissolution process that assists the Li intercalation/deintercalation process during potentiostatic charging and discharging conditions.

This report contains both the methodology to obtain surface modified active material for Li-ion batteries and characterization of the cathode material. Our aim was to enhance the performance of LMO based batteries by surface modification on a molecular scale (Appendix 1). We present here several coating methods along with their electrochemical performance. Investigation of SM-LMO cathode materials using various electrochemical and surface sensitive techniques has provided the information needed to understand the effect of the surface modification on the surface chemistry of the cathode in organic electrolyte.

Additionally, we present the development of a new strategy to study the effect of surface modification on the reactions at cathode/electrolyte interface, which are responsible for the capacity fading. The surface process was monitored by *in situ* electrochemical AFM under potential and temperature control using a new design for an electrochemical AFM cell (Appendix II). Direct observation of the surface under potential and temperature control provides a nanoscale understanding of the local redox reactions at cathode/electrolyte interface. The development of a high-resolution *in situ* EC-AFM method for battery studies at elevated temperature will enable us to speed up the process, to do predictive degradation studies and predict the battery properties. As an outcome of the EC-AFM image processing, we started to exploit the feature extraction capabilities of wavelets to enhance the information obtained from AFM images. We propose to develop further software tools that can be integrated with imaging equipment to provide users more insight towards understanding surface images.

Project Objectives

The overall objective of this project was to determine the feasibility of using lithium manganese oxide as a cathode material in rechargeable lithium ion batteries to achieve higher voltage, lower cost and increased safety.

Project objectives were to:

- Finalize the methodology for two surface treatments of the LMO cathodes.
- Determine the surface chemistry for each surface modified LMO cathode.
- Demonstrate that Mn dissolution can be reduced by 30-50 % in LMO cathodes.
- Demonstrate that capacity fading can be reduced by 30-50 % in LMO cathodes.
- Show from the research findings that a successful surface treatment can reduce the manufacturing cost of lithium ion batteries by 10-20 %.
- Investigate the effect of surface modifications on the reactions at cathode/electrolyte interface and on the mechanism of capacity fading.
- Surface characterization and statistical analysis, using wavelets.

Project Approach

Our approach to minimize surface degradation of LiMn_2O_4 by using surface modification on molecular scale has integrated several objectives and tasks as presented above. Besides concluding a reproducible procedure for surface treatments of the LMO cathodes, we studied the surface modification of the cathode by conducting detailed investigations of the electrochemical behavior and surface characterization by various surface structure sensitive techniques. In the following, the materials used in our experiments, sample preparation and characterization techniques are presented.

EXPERIMENTAL SECTION

MATERIALS

Cathode pellet was prepared from LiMn_2O_4 (synthesized by Mitsubishi Chemical Corp.), acetylene black (Denki Kagaku Kogyo Co. Ltd.), and Teflon (Mitsui Dupont Fluoro Chemical Co. Ltd.). The polymers poly(diallyldimethylammonium chloride) (PDDA) and Poly(styrene sulfonic acid) sodium salt (PSS) were purchased from Polysciences, Inc. (Warrington, PA). The buffer solution used throughout the experiments was Tris 8.5 (5 mM Tris buffer, pH 8.5, purged with N_2). The PDDA and PSS solutions were prepared in the Tris 7.2 buffer. The percentages used in this article are molar fractions unless otherwise stated. All chemicals were used as received without further purification. De-ionized water (resistivity $> 17.5 \text{ M}\Omega\text{-cm}$) was obtained from a Nanopure Reverse Osmosis Purification System from Barnstead (Dubuque, IA).

SAMPLE PREPARATION

Cathode pellets were routinely prepared by mixing 75 wt.% of LiMn_2O_4 , 20 wt.% of acetylene black, and 5 wt.% of Teflon, and were kneaded to a flat sheet with a mortar and a pestle. Then, the pellet was dried at 120°C in a vacuum oven for 2 hours to remove excess water and water vapor. We used various methods for applying the coating in order to find which procedure results in increased characteristics of the batteries. One method consisted in applying a polymer film on a cathode pellet and the other

method (with several manufacturing condition variables) consisted in applying a thin, molecular, film on the LiMn_2O_4 powder before cathode fabrication.

PDDA-coated pellet First, the cathode pellet was prepared as shown above. The PDDA coating was applied by pouring the PDDA solution of different concentrations (i.e. 10, 20, 30, 50 and 100 mM) over the pellet and left for 2 h. After the PDDA deposition, the pellet was removed from solution and rinsed in a buffer solution. Then, the coated pellet was dried at 120°C in a vacuum oven for 2 hours to remove excess water and water vapor, which could react with the electrolyte. The coated pellet was then pressed on an aluminum metal mesh and used as the working electrode in the electrochemical measurements.

PDDA-coated powder The powder was first weighted and then a 50 mM Tris 8.5 solution was poured over the powder. It was sonicated in order to disintegrate the agglomerated powder and increase the surface area available for polymer adsorption. After 2 h, a PDDA solution (10, 20, 30, 50, 100 mM) was added and slowly mixed using a stir bar for another 2 h. The powder was separated by centrifuge and dried for 2 h at 120°C . The powder was used to obtain cathode pellet using the method described above. We have tried several coating methods for the powder material since the order of coating steps is known to affect the mixing behavior. When the powder was mixed using a stir bar directly with the PDDA solution (either by pouring the PDDA solution over the powder or by adding the powder to the PDDA solution), the resulting powder after drying was agglomerated and sticky. The appearance of the powder was like thin, hard, flakes with very poor mixing properties. We could not make good cathodes out of this powder, so that we did not proceed to further investigations for this case.

SAMPLE CHARACTERIZATION

The PDDA amount adsorbed on pellet and LiMn_2O_4 powder has been obtained using a UV-Visible Spectrophotometer (Varian Analytical Instruments, CA). The PDDA amount adsorbed on LiMn_2O_4 powder and on the pellet from solutions with various PDDA compositions has been determined.

For electrochemical studies, a beaker-type three-electrode cell was used inside an Argon atmosphere glove box. The working electrode was placed in the cell with two pieces of pure Li metal (Alfa Aesar), which was used as the counter and the reference electrodes. The electrolyte used for electrochemical measurements contained 1 mol of LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC). The proportions for EC:DEC were 3:7 by volume (Mitsubishi Chemical Corp.).

Charge/discharge properties of the electrochemical cell were measured with a Model HJ-201B charge/discharge unit (Hokuto Denko Corp.) in the voltage range of 3.2 V and 4.3 V. Cyclic voltammetry was carried out with a Model AFCBP1 bipotentiostat (Pine Company) between 3.2 V and 4.4 V at the sweep rate of 10 mV/min. After charging, the cathode and a Li metal separated by a polyethylene sheet were placed in a Teflon bottle and immersed in fresh electrolyte, and stored in an oven at 70°C for one week. The cathode was then extensively rinsed with pure DMC. *Before* and *after storage*, the electrochemical properties of the cell were

determined. *After storage*, new Li metal was used to assemble the battery. All sample preparations and measurements were conducted at room temperature (25°C).

The surface of the cathode was observed by atomic force microscopy (AFM, Nano Scope IIIA, Digital Instruments) using various imaging modes in air and in electrolyte. Commercially available triangular gold-coated cantilevers with pyramidal tips of 0.05 N/m force constant were used for AFM imaging in contact mode. To correct for tilt and bow, images were typically processed using the imaging software of the instrument.

The electrochemical cell used in EC-AFM is similar to the cell used for other electrochemical measurements, e.g. it consists of cathode material as the working electrode and two lithium sheets as counter and reference electrodes. Active electrochemical control and simultaneous observations of the surface reactions will be carried out in the AFM set-up. We have already designed and constructed a set-up that allows us to image the cathode surface changes under potential/current control. The potential and temperature control under AFM in wet conditions is, however, a more complicated issue. The applied potential/current is monitored through a bipotentiostat and a thermostat controls the temperature of the sample that will be heated up by a small device, which has been specially designed to fit the AFM scanner head. The sample was attached to the holder using double-sided conductive tape. The electrochemical cell consists of glass and was placed over the sample. An O-ring sealed the electrolyte. The assembly of the cell has been performed inside the argon atmosphere glove box at room temperature. All measurements were conducted at room and elevated temperature. Galvanostatic discharge and charge curves as well as cyclic voltammetry have been measured prior to *in situ* EC-AFM.

In a typical EC-AFM experimental run the surface was first observed at a constant open-circuit voltage (OCV). Then, the surface was monitored under potential control at different potential values within the range from 3.2 to 4.5 V vs. Li/Li⁺ in LiPF₆ electrolyte in order to image the changes in surface structure and topography of the cathode during charging and discharging process. The surface scans were performed at several resolutions in order to analyze both global and local information.

Energy Dispersive X-ray analysis was carried out on an Oxford Link 1000 Scanning Electron Microscope (SEM) with an Isis EDS detector with a beryllium window and 139 eV resolution. All data were taken under the same conditions to avoid scaling issues.

Transmission Electron Microscopy has been performed on a Topcon 002B, 200KV. Transmission Electron Microscopy (TEM) was used to study the PDDA coating on nanoparticles. We used 2 methods for dispersing the powder for TEM observation. In the first method, the powder was mixed in methanol solution and ultrasonicated for two hours, and then transferred on holey carbon coated copper TEM grid. The resulted powder was agglomerated and thus not suitable for TEM observation. The second method consisted of grinding the powder in methanol solution and then transferred on holey carbon coated copper TEM grid.

Project Outcomes

UV Spectroscopy

UV-vis spectroscopy has been performed in order to monitor the adsorption of PDDA on cathode pellet and LiMn_2O_4 powder. Table 1 presents the PDDA amount adsorbed on pellet and LMO powder. The variation of the PDDA amount adsorbed on pellet and on powder with the initial PDDA concentration in solution follows a parabolic law. The maximum amount of PDDA adsorbed in both cases is located in the concentration range from 30 to 60 mM PDDA.

Electrochemical measurements

The electrochemical tests have been performed on both types of samples, i.e. samples obtained by applying a PDDA film on a cathode pellet and samples obtained by applying a thin, molecular, film on the LiMn_2O_4 powder. Charge/discharge properties of the electrochemical cell were measured *before* and *after storage*. The electrochemical properties of the cathode were first determined *before storage*. These results were reproducibly obtained in a subsequent set of *before* and *after storage* experiments. The *after storage* measurements refers to data collected on samples after storage in a charged state at 70°C for one week.

For comparison, cyclic voltammetry and charge/discharge curves of LMO based cathodes are presented in Figs. 1, 2. In order to find the concentration range of PDDA in the coating solution, several electrochemical measurements have been initially performed. Figure 3 presents charge/discharge curves and the variation of the measured capacity with the number of cycles for the cathodes obtained from SM-LMO powder in 10, 50, and 200 mM PDDA solution. For large PDDA concentrations, e.g. 200 mM PDDA, the capacity is even lower than the initial LMO based cathode and the interfacial resistance is high. Therefore, we have further explored only the PDDA concentration range from 10 to 100 mM PDDA solutions.

Capacity measurements were first performed for all types of samples, i.e. polymer-coated cathode pellets and cathodes made of PDDA coated LiMn_2O_4 powder (Figs. 3, 4). The capacity of the new cathodes is generally good, within the range of LiMn_2O_4 -based cathodes obtained in our group. Superior values were obtained for coated pellets, but the capacity values do not seem to be proportionally related to the PDDA amount absorbed on the surface. This is probably because of the difference in initial permeability of the pellets that dictates the ability of the solution to reach all the particles.

The stability of capacity after 5-10 cycles depends on the coating method (Figs. 5, 6). For the coated pellet, the cathode lost about $4.3 \pm 1.1\%$. The capacity lost was higher for the coated powder, i.e. $9.3 \pm 5.3\%$. The reason for higher capacity loss of the coated powder might be the difference in mixing properties of the coated powder.

The electrochemical tests *before* and *after storage* is presented in Figs. 7-11 for the PDDA coated LMO-based cathode and in Fig. 12-16 for the PDDA coated SM-LMO based cathodes. Generally, the charge/discharge curves of the uncoated LiMn_2O_4 -based cathode after storage have shown 18-20 % loss of the initial capacity (Fig. 2). After one week of storage, the discharge capacity measured at the same current density decreased. In addition to the capacity fading, hysteresis between charge and discharge curves became larger after storage. Since the hysteresis corresponds to the resistance of the cell, it is clear that after storage the resistance of the spinel cathode increased.

Coating the cathode pellet or the LiMn_2O_4 powder resulted in an improved stability of the coated cathode during charge/discharge cycling in organic electrolyte at room temperature (Figs. 5, 6). After storage, the capacity fading has been significantly reduced. Capacity lost after storage was about 12 and 6% for PDDA-coated cathode pellet and PDDA-coated LiMn_2O_4 powder, respectively. In the case of PDDA-coated cathode, the capacity fading decreases as PDDA concentration increases. The hysteresis between charge and discharge curves became larger after storage, this behavior being similar to the uncoated LiMn_2O_4 -based cathode. In case of cathodes made of PDDA-coated LiMn_2O_4 powder, the capacity fading has shown a minimum value for cathodes obtained from powder coated in solution containing 30 and 50 mM PDDA. Although the hysteresis between charge and discharge curves became larger after storage, the magnitude of the displacement is lower than that measured on PDDA-coated cathode pellet. Moreover, the capacity curve obtained after storage for cathodes made of powder coated in solution containing 30 mM PDDA has retained the aspect before storage.

Transmission Electron Microscopy

Transmission electron microscopy has been used to characterize the polymer coating on the LiMn_2O_4 particles. We used 2 methods for dispersing the powder for TEM observation. In the first method, the powder was mixed in methanol solution and ultrasonicated for two hours, and then transferred on holey carbon coated copper TEM grid. The resulted powder was highly agglomerated, making the TEM observation of the PDDA coating very difficult. The second method consisted of grinding the powder in methanol solution and then transferred on holey carbon coated copper TEM grid. Figures 17 and 18 shows the TEM images of the PDDA coated particles for two PDDA concentrations, i.e. 30 and 100 mM PDDA, respectively. In order to correlate the characteristics of the polymer coating with the electrochemical properties of the cathode made of polymer-coated nanoparticles, we performed extensive observation by TEM. The TEM observation revealed the existence of the polymer. However, it is not clear if the polymer coating is uniform or not. We performed additional investigations using the Scanning Electron Microscopy (SEM) to characterize the polymer coating.

Electrochemical Atomic Force Microscopy

The surfaces of the cathode were observed by atomic force microscopy (AFM, Nano Scope IIIA, Digital Instruments) in wet and dried state. We investigated the effect of surface reaction at the cathode/electrolyte interface on the mechanism of capacity fading at elevated temperatures by *in situ* Electrochemical Atomic Force Microscopy (EC-AFM).

First, the cathode surface was imaged in dried state. Figures 19 and 20 show the AFM in air in contact mode of cathode surface in air, at various scan sizes. Samples were obtained from PDDA coated LMO powder in solution containing 30 and 100 mM PDDA. The cathode surface looks smooth and homogeneous, typical to a well-mixed composite material. However, for high PDDA concentration, i.e. 100 mM PDDA, several “lake”-like spots were observed (Fig. 20, scan size $7.08 \times 7.08 \mu\text{m}$). These spots are likely areas containing PDDA in excess.

In the presence of the electrolyte, the binder and active material areas were identified by comparing particular topography of each phase present in the surface with that observed in air. We studied the local redox reaction by *in situ* EC-AFM imaging of the cathode surface in organic electrolyte under potential control at room temperature and elevated temperature. We investigated the effect of surface reaction at the cathode/electrolyte interface during a charging/discharging cycling. Figure 21 and 22 show the *in situ* EC-AFM of SM-LMO based

cathode (30 mM PDDA solution) in 1 M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at room temperature. A sketch of the potential variation was inserted to help understanding the EC-AFM image acquisition. In this case, no significant changes in surface topography have been detected. Figure 22 shows the *in situ* EC-AFM of SM-LMO based cathode (30 mM PDDA solution) in 1M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at elevated temperature (55 °C). The stability of the surface topography is noteworthy, which explains the electrochemical behavior observed after storage (Fig. 14). Figure 23 shows the *in situ* EC-AFM of SM-LMO based cathode (100 mM PDDA solution) in 1M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at room temperature. Slightly unstable, the cathode surface shows an increase in surface roughness during charging and a smoothing trend during discharging. This is consistent with the delithiation-lithiation reaction that relates to the charging/discharging process but the changes in surface topography are significant at this observation scale. Figure 22 shows the *in situ* EC-AFM of SM-LMO based cathode (100 mM PDDA solution) in 1M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at elevated temperature (55 °C). Significant and irreversible changes take place during charging, which clearly account for the decrease of the measured capacity after storage (Fig. 16).

Further quantitative characterization of the changes taking place on the cathode surface can be obtained from roughness analysis. Surface roughness is an important characteristic of surface topography that can help compare different surfaces and reveal underlying features. It is often difficult to make such comparisons based on raw SPM images and calculated Root-Mean-Square (RMS) roughness and Power Spectral Density (PSD). Since RMS roughness is a standard deviation of surface heights, it is appropriate to calculate RMS only for stationary roughness. In the same way, PSD based on Fourier Transform assumes stationarity and calculates the power spectrum of image profiles across the whole range. A drawback of Fourier power spectrum is that it is not localized in space (or time), i.e. it does not provide information about the location of different frequencies. Thus, if the roughness is not stationary (i.e. the roughness mean is not constant or different frequencies are not present at the whole range of a given space), RMS and PSD based on the raw AFM image are not capable of providing correct information about surface roughness and its features. Here we introduce the wavelet transformation, which has the capability of time-frequency localization. As opposed to Fourier transformation that identifies key frequency components in a signal, wavelet transformation can also provide a temporal (or spatial) resolution of the frequency information. This makes it an ideal tool to detect trends and discontinuities [4]. In image analysis, wavelet transformation can capture patterns at all relevant frequency scales, thus providing a level of detail that may not be possible otherwise. On the other hand, Wavelet Transform (WT), which is localized in space (or time), gives frequency information at different frequency scales and allows a multiscale description of surface morphology. RMS roughness can also be calculated at different scales, thus making the analysis qualitatively and quantitatively superior. We propose further to develop software that provides statistical analysis of the data. Statistical analysis of the wavelet data set can be carried out efficiently since the image data have been transformed into wavelet functions. Statistics are expressed in mathematical relationships and the computation of statistical results is simplified with data in functional form. This technique has a great potential in all microscopy studies, where localized information has to be quantified.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX)

High resolution SEM combined with EDAX offer detailed information on both morphological and compositional aspects of the coated particles. Figures 25-30 present the EDAX data along with the SEM images of PDDA and PSS coated powder samples. The Mn and O peaks are clearly visible rising above the characteristic Brongstrum peak. Manganese and oxygen distribution maps are also presented. Additionally, we mapped the particles for elements such as C, which is contained in PDDA and PSS but not in nanoparticles. The carbon distribution is very weak but in agreement with the low amount of PDDA existing on particles. There are slight differences between the amounts of C present on LMO particles of different sizes. For comparison, the EDAX data for small and large particles is presented in Fig. 31. The amount of PDDA on small particles is bigger than on large particles due to the fact that small particles have a larger surface area and, consequently, adsorbed a larger amount of polymer. It is interesting to observe that the sample containing 30 mM PSS shows no adsorption on large particles (Fig. 29).

Hypothesis: The significant improvement of thermal stability of Li-ion batteries by polymer coating of LiMn_2O_4 is probably due to the “membrane” like behavior of the polymer coating. The coating protects the LiMn_2O_4 particle surface from the full contact with the electrolyte and possibly blocks surface reactions that are responsible for capacity fading in Li-ion batteries. Our previous results are consistent with a possible degradation mechanism wherein the LiPF_6 salt dissociates reversibly to LiF and PF_5 . The PF_5 can in turn react with the manganese oxides on the surface to form manganese difluoride on the cathode and soluble products in the electrolyte. The soluble products in the electrolyte could be POF_3 and PO_2F_2 (Appendix III). Thus, the protection conferred by the polymer coating yields to improved thermal stability of Li-ion batteries.

Conclusions

- Coating with a polymer film successfully modified LiMn_2O_4 nanoparticles used as active material in cathode fabrication. The coating method is sensitive to the initial powder dispersion and mixing procedure.
- TEM, SEM and EDAX analyses have confirmed the polymer coating. These techniques support the formation of a thin polymer film on the surface of LiMn_2O_4 nanoparticles,
- Coating the cathode pellet or the LiMn_2O_4 powder results in an improved stability of the coated cathode during charge/discharge cycling in organic electrolyte at room temperature.
- The measured capacity fading after storage decreased for coated cathode pellet and LiMn_2O_4 powder. Capacity fading measured on cathodes made of PDDA-coated LiMn_2O_4 powder was very small for cathodes obtained from powder coated in solution containing 30 and 50 mM PDDA.
- The *in situ* AFM observation of the cathodes at room temperature shows changes in surface topography that follow the potential cycle. These are attributed to the lithiation/delithiation process that accompanies the change in potential during a charge-discharge cycle.
- Our hypothesis is that the polymer layer blocks surface reactions that cause degradation.

Recommendations

- Coating the cathode pellet or the LiMn_2O_4 powder results in an improved stability of the modified cathode during charge/discharge cycling in organic electrolyte at room temperature. However, the amount of the PDDA has to be optimized to yield maximum stability of the modified cathode.
- Changes in surface topography that follow the potential cycle were attributed to the lithiation/delithiation process that accompanies the change in potential during a charge-discharge cycle. These changes are related to either Mn^+ dissolution or film formation on the cathode surface but the nature of the film is not yet established. The actual mechanism of capacity fading needs further investigations. Although the complex reactions that take place on the cathode surface have not been completely elucidated, the improvement in battery performance demonstrates that the coating method proposed in this research
- Development of new image processing techniques for studying the local changes in surface topography

Public Benefits to California

This project is a successful attempt to develop high energy density, fast, inexpensive and environmentally friendly novel rechargeable batteries. Almost all-commercial Li-ion cells are presently based on the carbon/liquid electrolyte/LiCoO₂ redox system that shows a high capacity and stable performance but is expensive and toxic. Lithium manganese spinel LiMn₂O₄ as a possible candidate for LiCoO₂, did not hit the market yet due to its poor cycling stability and less capacity, especially at elevated temperatures (55-60 °C). Due to the hot weather in California, reducing the self-discharge at high temperature was a challenge to the success of the spinel-based Li-ion technology, i.e. to prepare optimum materials from a capacity and cycling standpoint of view. We succeeded in obtaining novel cathodes based on LiMn₂O₄ that show an excellent stability at elevated temperature.

There is a number of energy, economic, and environmental benefits concerning the development of LiMn₂O₄ batteries used for energy storage and power quality systems. The potential impact to the consumers is revealed by the low raw materials price for manganese oxide (\$2.29/kg) compared to cobalt oxide (\$39.6 to 41.8/kg) [30]. This translates into the cost of the active material of about \$0.5 for manganese oxide and \$ 8 for cobalt oxide per 1000 cathodes, i.e. a reduction in the cost of about 93.75%. Besides lower costs, these batteries can be used as stable source of energy for vehicle [31], and for uses in homes and industry. For instance, a solar generating system with batteries supplies electricity when it is needed. Storing electrical energy makes photovoltaic (PV) systems a reliable source of electric power day and night, rain or shine, and even during a storm-related power outage or rolling blackout. Customers generate their own electricity by solar power and can sell excess electricity to CA utilities. PV systems with battery storage are being used all over the world to power lights, sensors, recording equipment, switches, appliances, telephones, televisions, and even power tools. These batteries can be used for marine applications, in solar marine power systems that replace noisy generators giving also an independent power source fueled by the sun marine power. The PV systems are not the only ones that can take advantage of an extended lifetime and improved performance of the battery. Besides the solar power, there are other alternative energy such as wind and hydroelectric power that will profit from using energy storage and power quality systems.

The concept behind a battery storage system is to store electrical energy for dispatch when its use is more economical, strategic, or efficient. From the utility grid, the battery systems can store off-peak energy and return it on demand as needed. From battery stands to modular battery storage systems, all the batteries are design to meet the needs of industry and customers, i.e. to provide innovative battery energy storage and power quality systems that improve the reliability and lower the cost of electric power. This based quality power solutions save space for revenue-producing operations while reducing power production costs. The incorporation of the battery systems can provide greater utility grid stability by serving as a controllable, demand-side management option that provides customers improved power quality and uninterruptible power. By storing electrical energy, the utilities can ensure reserve power requirements, defer new power plant construction, provide support for existing transmission and distribution systems, and maintain the level of reliability and power quality that customers need and expect. The widespread introduction of battery storage systems by utilities could also benefit the U.S. economy by more than \$26 billion by 2010.

Development Stage Assessment

Development Assessment Matrix

Stages	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop- ment	5 Product Develop- ment	6 Demon- stration	7 Market Transfor- mation	8 Commer- cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

- **Marketing**

This project is a successful attempt to develop high energy density, fast, inexpensive and environmentally friendly novel rechargeable batteries. Lithium ion batteries are ideal for storage because high-energy concentration of available power and find applications in many fields, such as:

- **Defense:** there is high interest in using Li-ion batteries as electrochemical power sources for safer and longer military operations, i.e., lighter-weight and longer-lived devices.
- **Energy:** - energy storage in independent electricity generation systems using solar energy and other forms of alternative energy generation. We have established contacts with BP Solar in Fairfield, CA and with Mitsubishi Chemical in Mountain View, CA.
 - these batteries can be used as stable source of energy in homes and industry. For instance, a solar generating system with batteries supplies electricity when it is needed. Storing electrical energy makes photovoltaic (PV) systems a reliable source of electric power day and night, rain or shine, and even during a storm-related power outage or rolling blackout. Customers generate their own electricity by solar power and can sell excess electricity to CA utilities. PV systems with battery storage are being used all over the world to power lights, sensors, recording equipment, switches, appliances, telephones, televisions, and even power tools.
 - battery storage systems that store electrical energy for dispatch when its use is more economical, strategic, or efficient.

- **Transportation:** these batteries can be used as stable source of energy for vehicle (electric vehicles). For marine applications, in solar marine power systems that replace noisy generators giving also an independent power source fueled by the sun marine power. The PV systems are not the only ones that can take advantage of an extended lifetime and improved performance of the battery. Besides the solar power, there are other alternative energy such as wind and hydroelectric power that will profit from using energy storage and power quality systems.

We will prepare a white paper on our results and send it out to battery companies.

- **Engineering/Technical**
 - Conducted extensive literature review on the problem of cathode degradation in Li-ion cells.
 - Conducted capacity measurements of Li-ion batteries over cycles and elevated temperatures Identified degradation of performance: surface reactions cause formation of MnF_2 film in surface and loss of Mn ions.
 - Defined a specific strategy of surface modification that change the nature of cathode degradation
 - Identified polyions PDDA and PSS as first candidates for surface coatings.
 - Successfully modified $LiMn_2O_4$ nanoparticles (used as active material in cathode fabrication) by coating with a polymer film.
 - Confirmed polymer coating by TEM, SEM and EDAX analyses; these techniques support the formation of a thin polymer film on the surface of $LiMn_2O_4$ nanoparticles,
 - Obtained improved stability of the coated cathode during charge/discharge cycling in organic electrolyte at room temperature and elevated temperature.
 - Identified further research issues for the best battery capacity performance
 - Published results in process.
- **Legal / Contractual**

Latest literature does not describe PDDA adsorption on $LiMn_2O_4$ particles. In order to get the information out to the public as soon as possible, we will not apply for a patent. We prefer open dissemination of our research results. We will publish results in key journals that have largest scientific audience in the subject area, so that all interested parties have access to the results. Identify (e.g. Chemistry of Materials).

- **Risk Assessment / Quality Plans**

Our research was focused on surface modification of the active material by polymer coating on the surface of $LiMn_2O_4$ nanoparticles in order to replace the toxic Co compounds with the more environmental benign Mn compounds. However, manganese (Mn) based battery degrades with cycles and a process to improve battery performance is critically needed. We selected surface coatings that are nontoxic such as polyion polymers and identified and developed safe and nontoxic procedure to coat. PDDA appears to be non-toxic and is an ideal material for coating treatment.

- **Strategic**

Short term:

- obtain convincing, irrefutable results that surface modification improves Li-ion cell performance.

Long term:

- identify processes that Li-ion manufacturers can use to switch over to production of manganese-based batteries.
- identify surface modification on other systems that employ electrochemical reactions, e.g. compound synthesis, have been shown to be effective in changing side reactions.
- identify other producers of batteries in California.
- continue to build relationships with Lithium-ion battery producers.
- design and implement a web page that displays recent research results.
- contact producers and educate them on advantages of changing to manganese batteries that have surface modified cathodes.
- provide new data with documentation to Lithium-ion battery producers and follow up to get feedback.

- **Production Readiness**

- Work with manufacturers in California.
- The new cathode material can easily replace the existing LiCoO₂ based cathodes for Li-ion batteries.
- Build a relationship with Mitsubishi Chemical Research and Innovation Center in Mountain View, CA.

- **Public Benefits / Costs**

- Manganese based Li-ion batteries are inexpensive and non-toxic. It is an ideal system to replace the toxic and expensive Co-based cathodes.
- Improve performance of LiMn₂O₄ based Li-ion batteries so that they can be used over many cycles at elevated temperatures.
- Reduction in material cost.
- Improvement in energy delivery of battery

- **Further Stages (#4-#8) for the future**

- We are prepared to conduct additional research, technology development, product development, demonstration, market transformation and commercialization if additional funds can be provided to our research team.

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Appendices

Appendix I Surface Modified LiMn_2O_4 -based Cathode

Appendix II Electrochemical atomic force microscopy (EC-AFM) cell set-up for studying the cathode surface under applied potential

Appendix III Proposed Mechanism of Degradation

Table 1 The PDDA amount adsorbed on pellet and LiMn_2O_4 powder.

pellet (8 mg)

ci (mM)	cf (mM)	PDDA amount ads on pellet [mol/g]
10	9.92	4.48E-09
20	18.82	6.84E-08
30	29.10	7.12E-08
50	48.25	9.06E-08
100	98.75	5.79E-08

powder (0.2 g)

ci (mM)	cf (mM)	PDDA amount ads on powder [mol/g]
10	0.46	5.53E-07
20	4.14	9.17E-07
30	10.82	1.09E-06
50	34.58	8.00E-07
100	97.56	1.13E-07

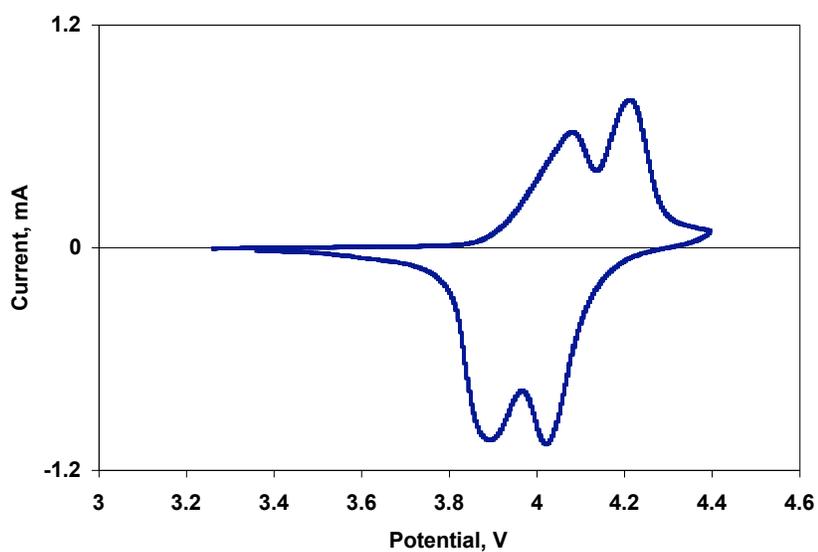


Figure 1 Cyclic voltammety of LMO-based cathode in 1 mol of $\text{LiPF}_6 + \text{EC/DEC}$

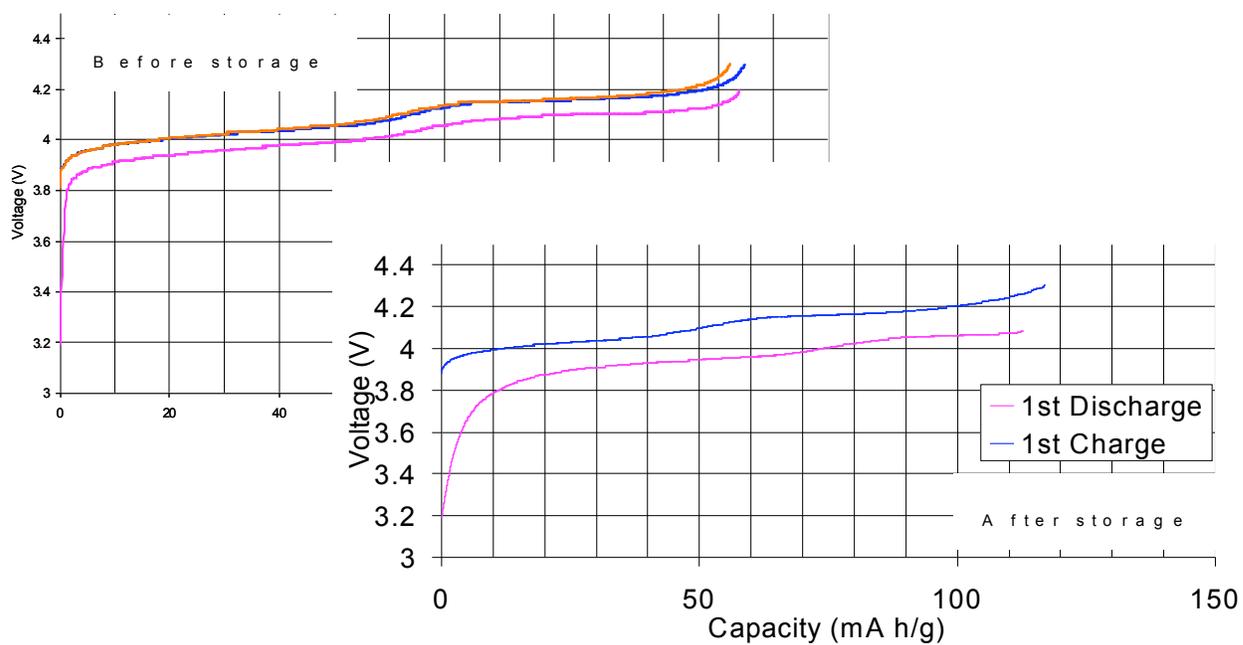


Figure 2 Charge/discharge curves and of LMO-based cathode in 1 mol of $\text{LiPF}_6 + \text{EC/DEC}$.

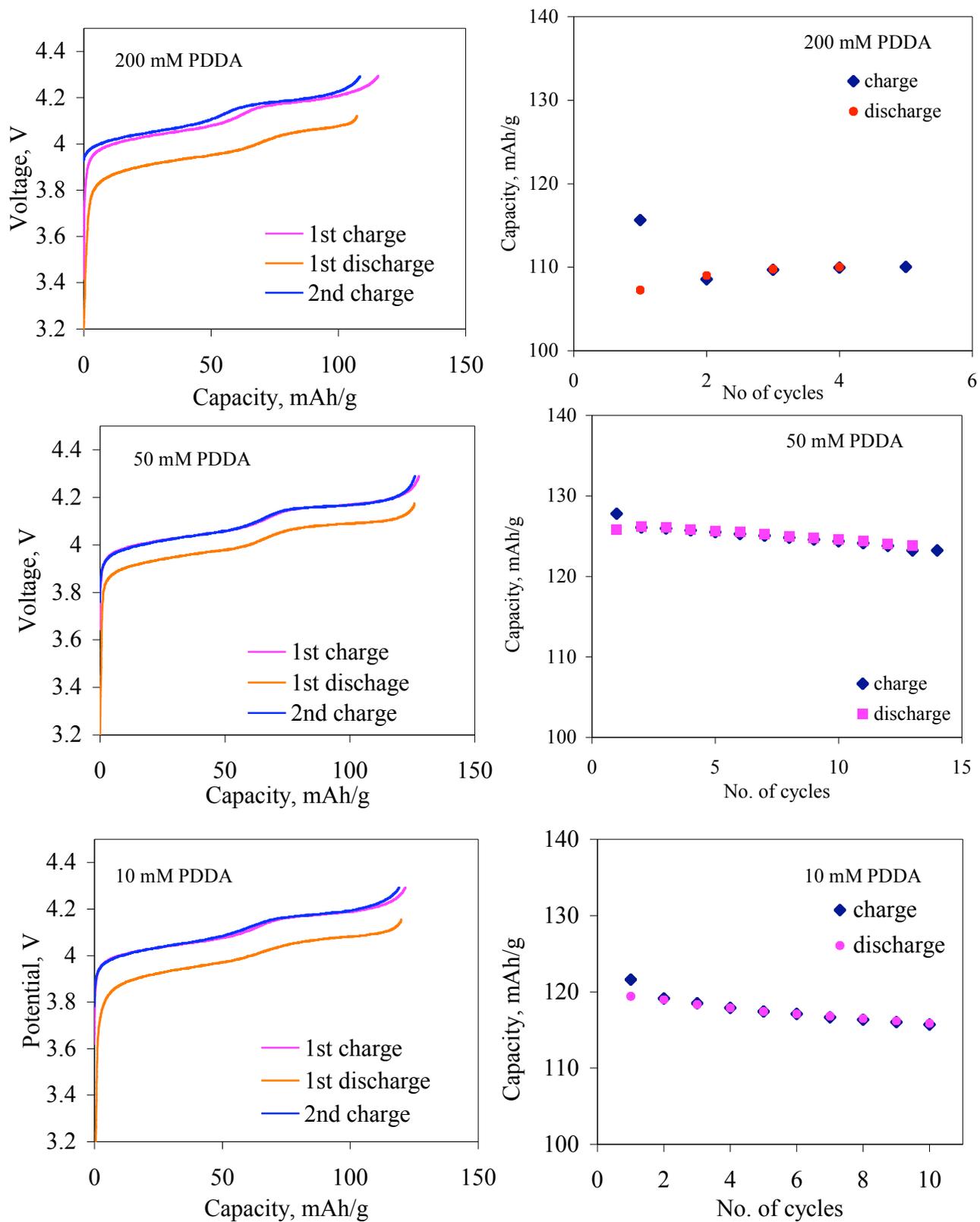


Figure 3 Charge/discharge curves (left side) and the variation of the measured capacity with the number of cycles (right side) for the cathode obtained from the PDDA coated powder.

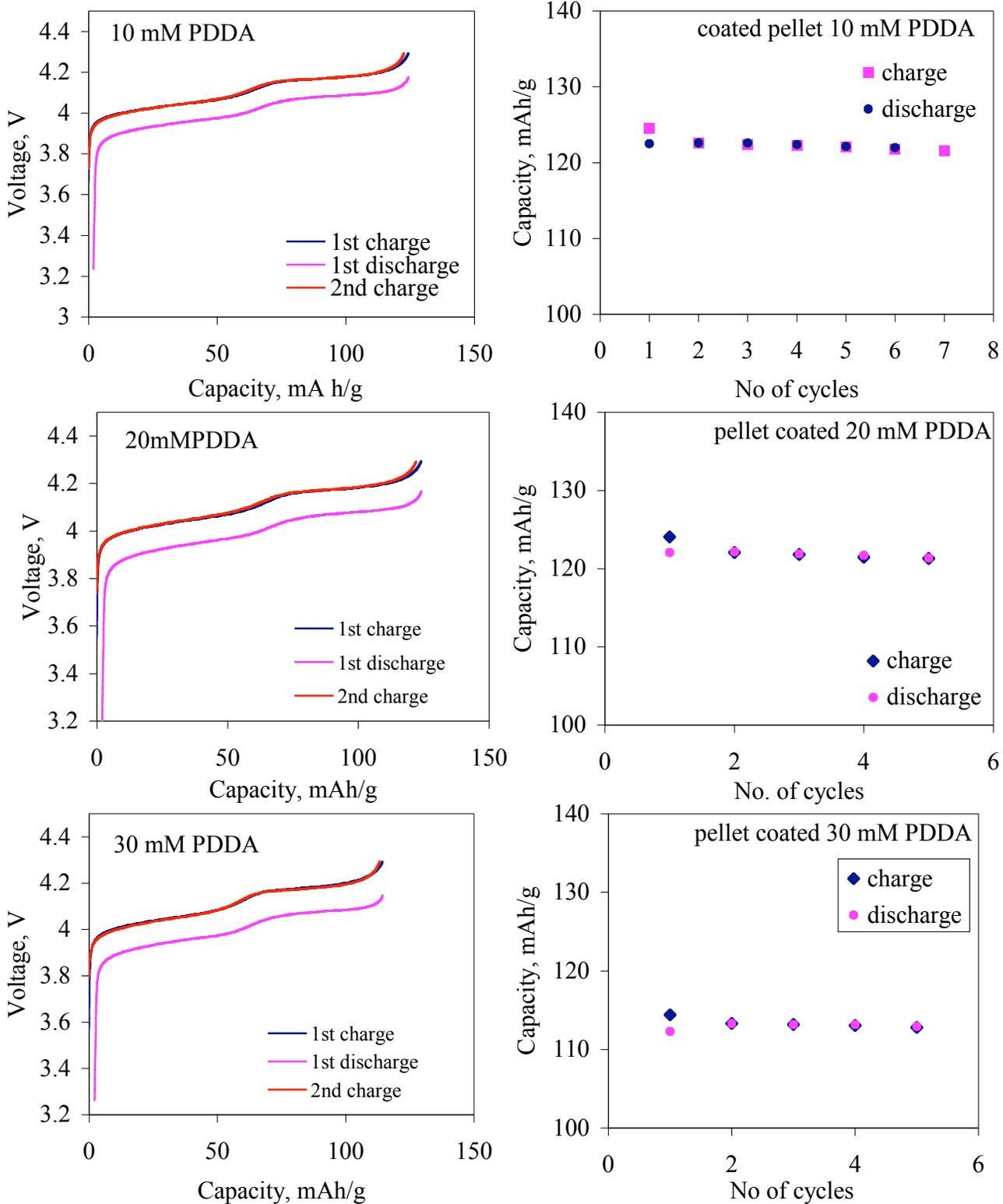


Figure 4 Charge/discharge curves (left side) and the variation of the measured capacity with the number of cycles (right side) for the PDDA coated pellets.

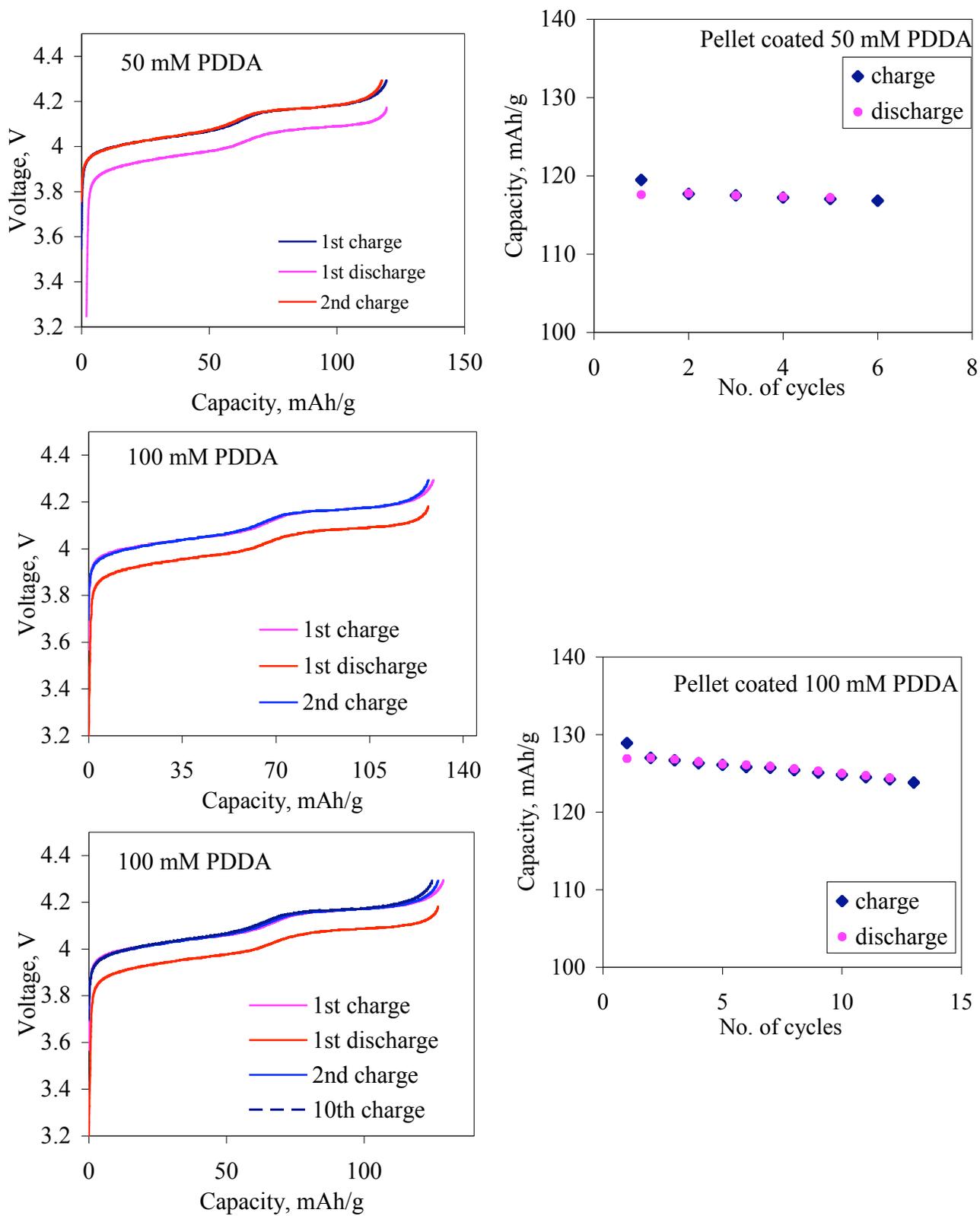


Figure 4 (continued) Charge/discharge curves (left side) and the variation of the measured capacity with the number of cycles (right side) for the PDDA coated pellets.

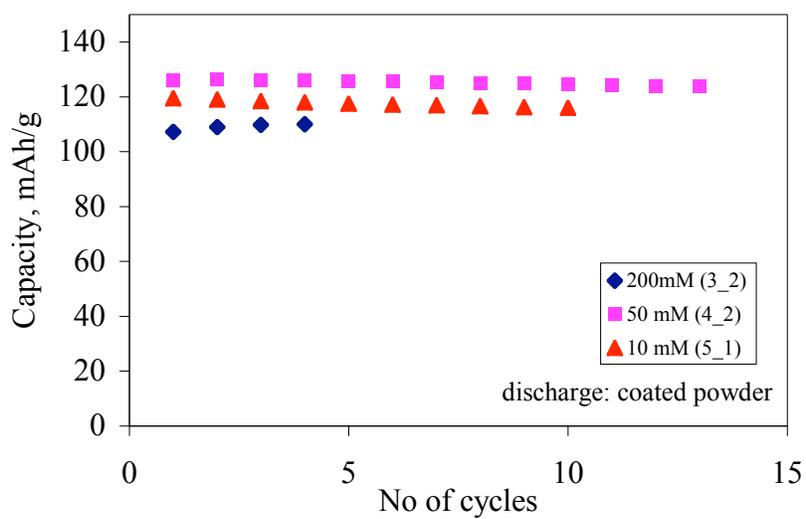
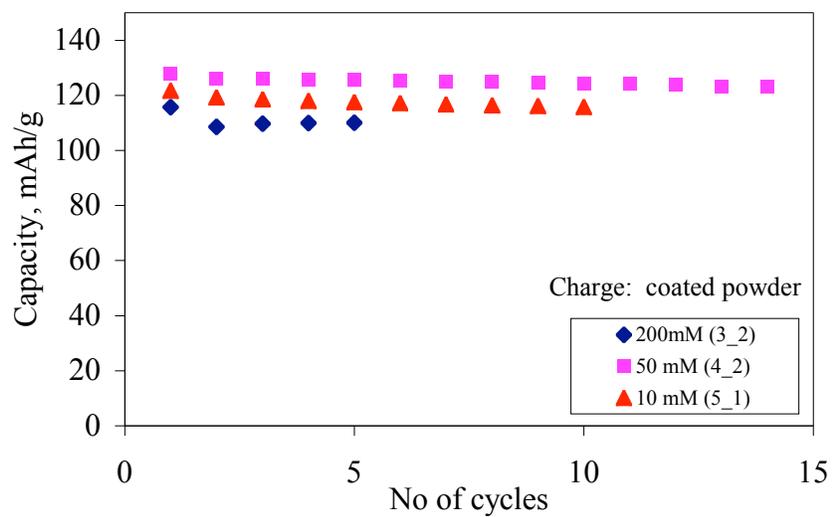


Figure 5 The variation of the measured capacity with the number of cycles for the cathodes obtained from the PDDA coated powder.

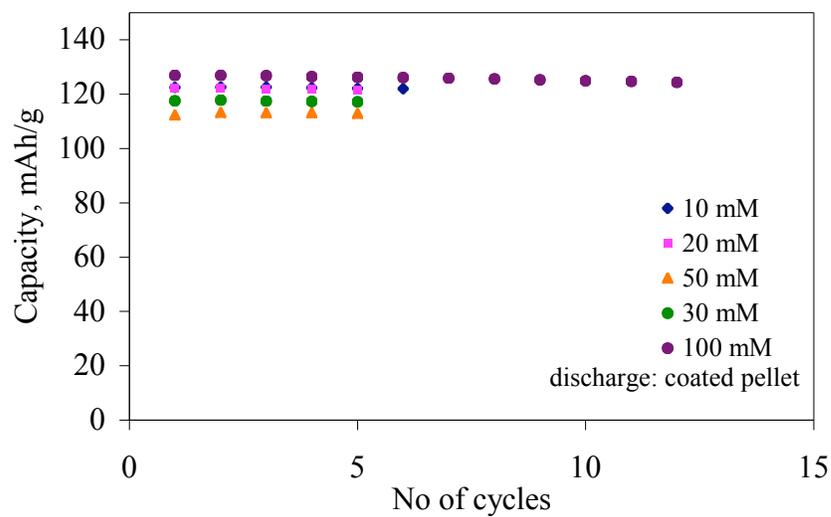
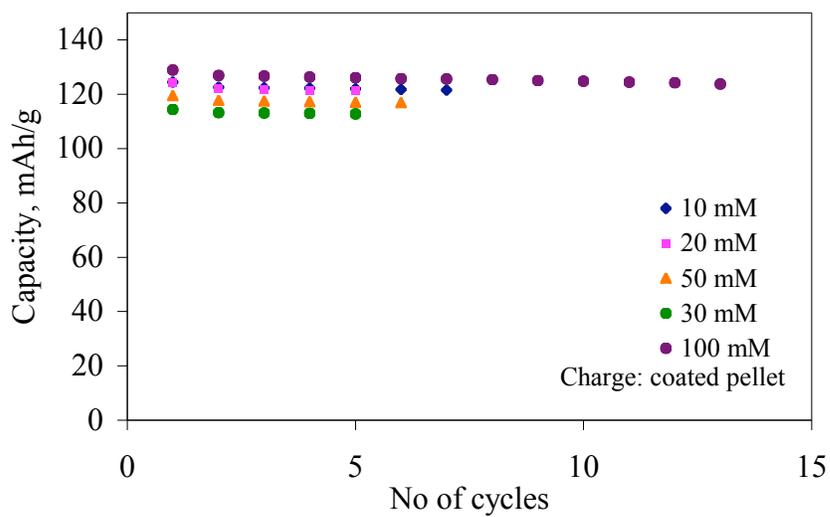


Figure 6 The variation of the measured capacity with the number of cycles for the cathodes obtained from the PDDA coated pellets.

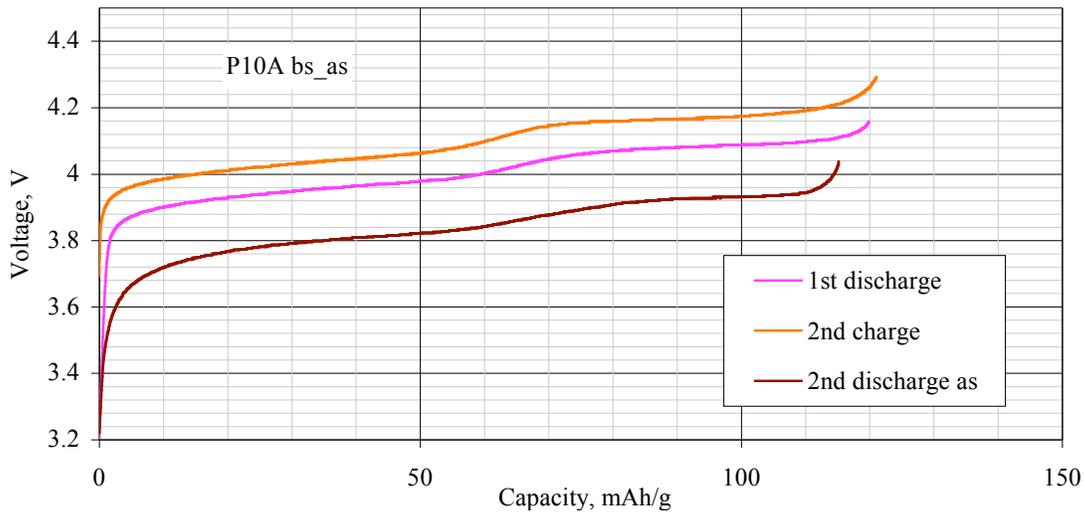


Figure 7 Charge/discharge curves of 10 mM PDDA coated LMO-based cathode before and after storage

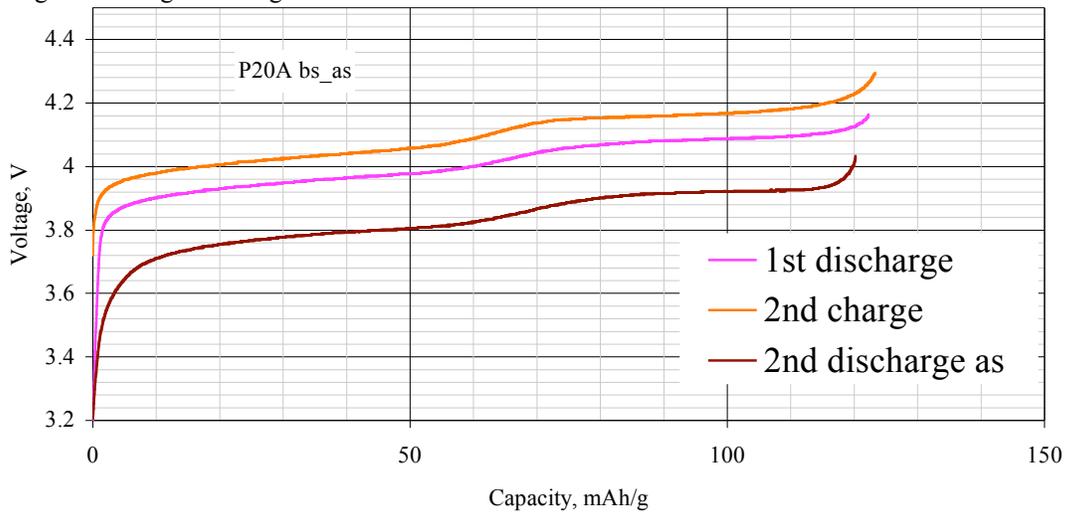


Figure 8 Charge/discharge curves of 20 mM PDDA coated LMO-based cathode before and after storage

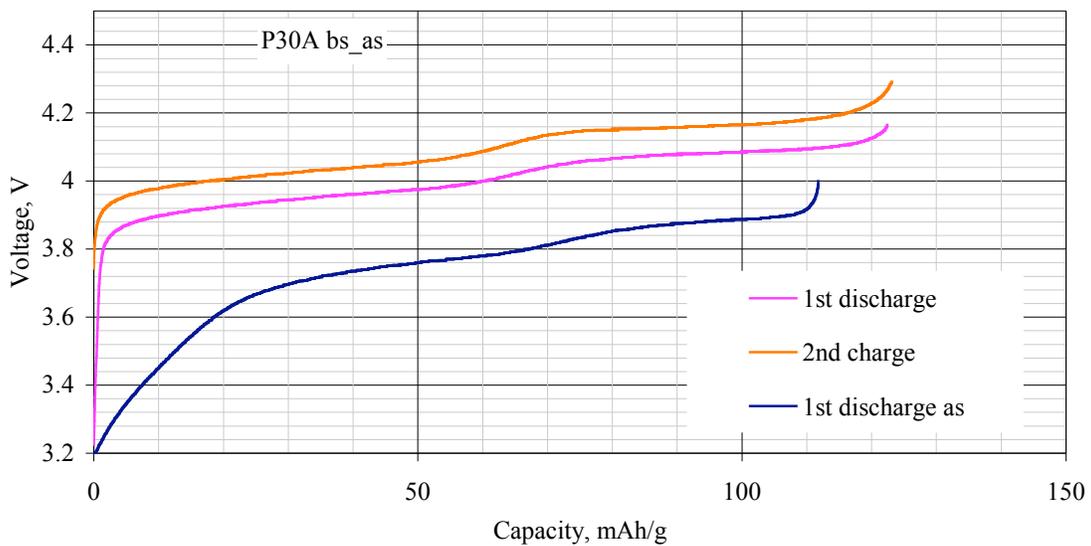


Figure 9 Charge/discharge curves of 30 mM PDDA coated LMO-based cathode before and after storage

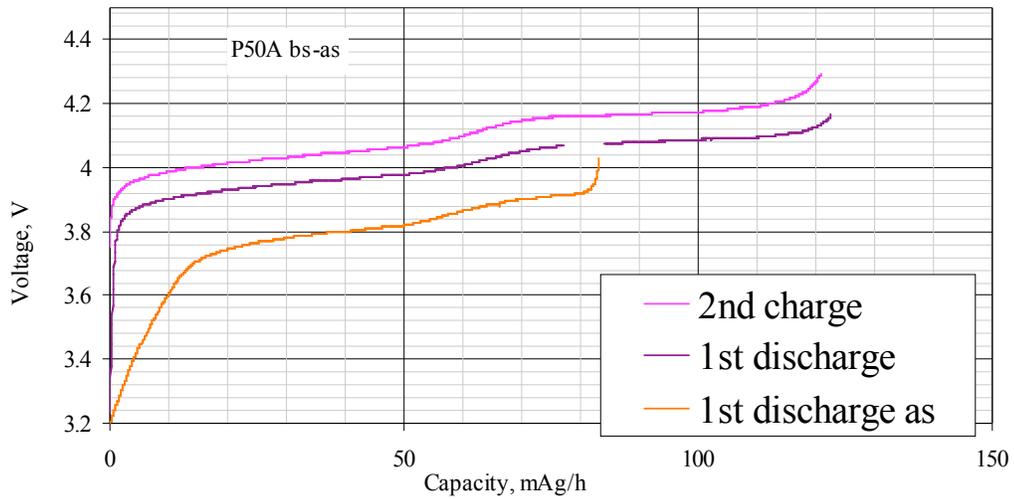


Figure 10 Charge/discharge curves of 50 mM PDDA coated LMO-based cathode before and after storage

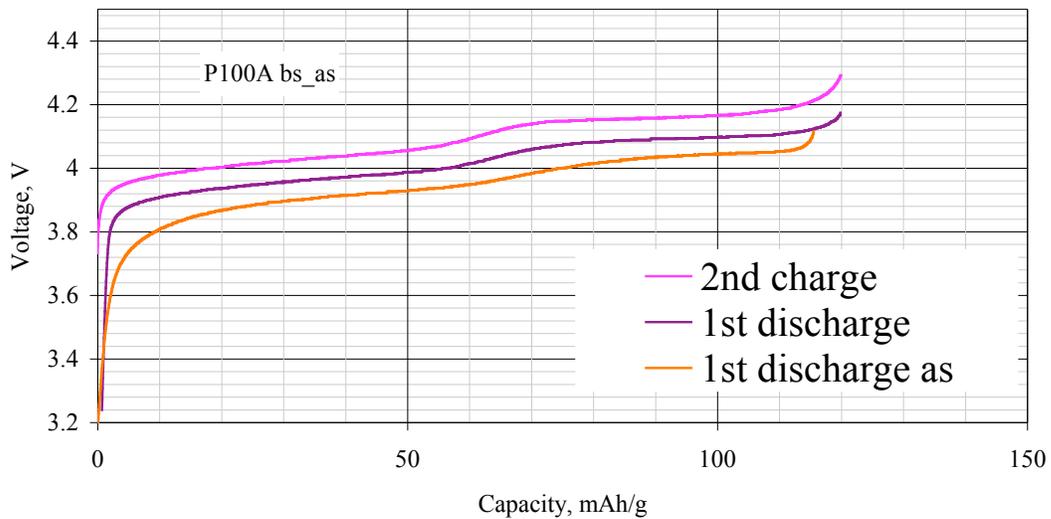


Figure 11 Charge/discharge curves of 100 mM PDDA coated LMO-based cathode before and after storage

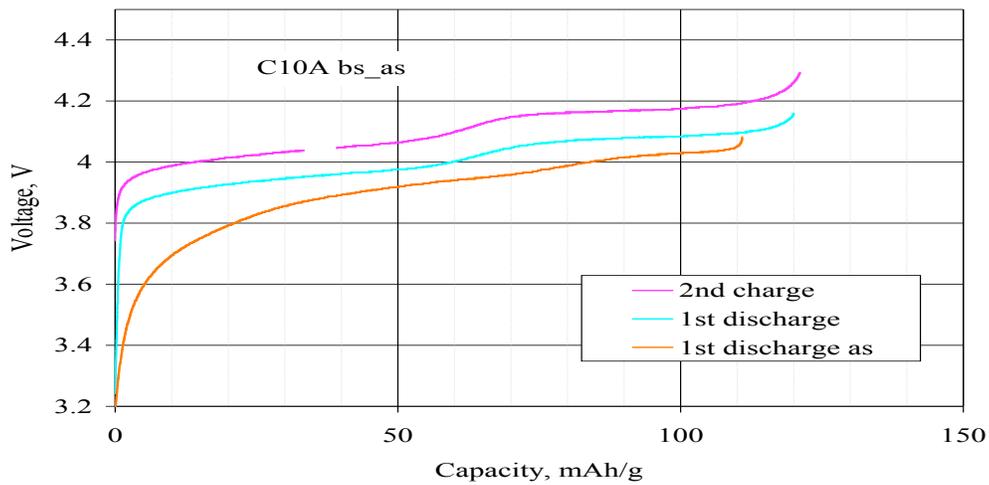


Figure 12 Charge/discharge curves of SM-LMO (10 mM PDDA) -based cathode before and after storage

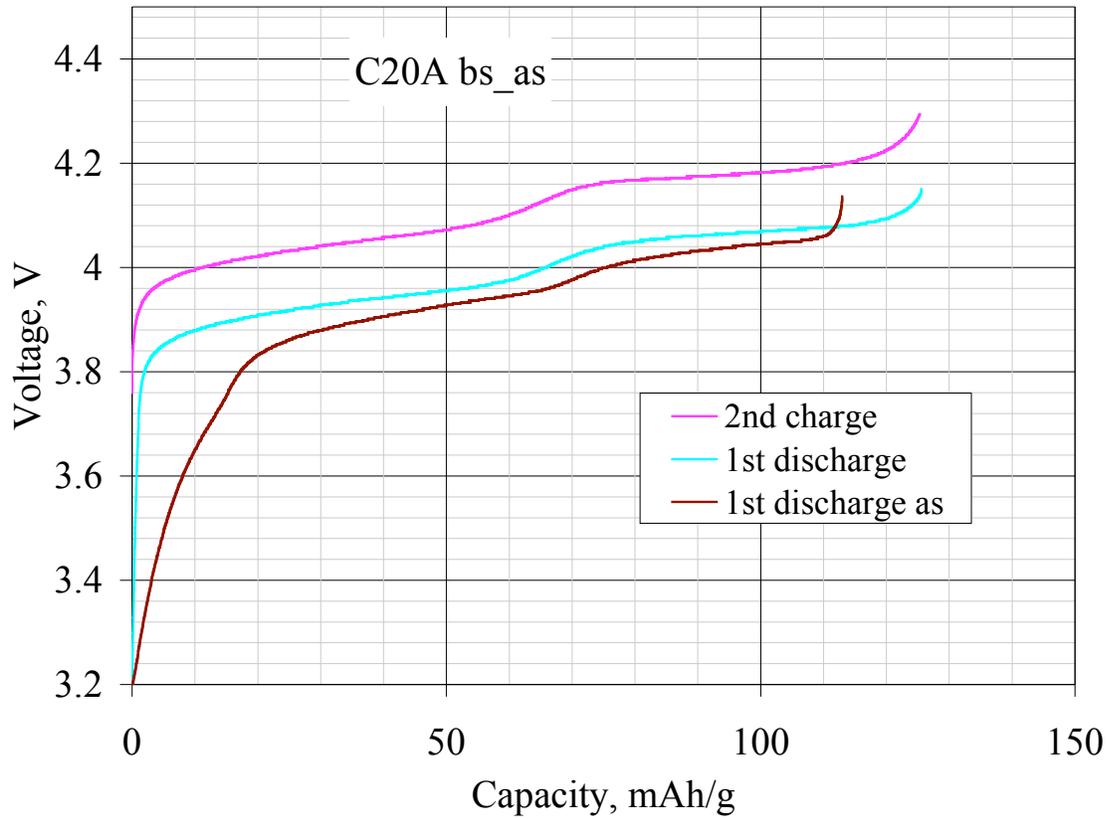


Figure 13 Charge/discharge curves of SM-LMO (20 mM PDDA) -based cathode before and after storage

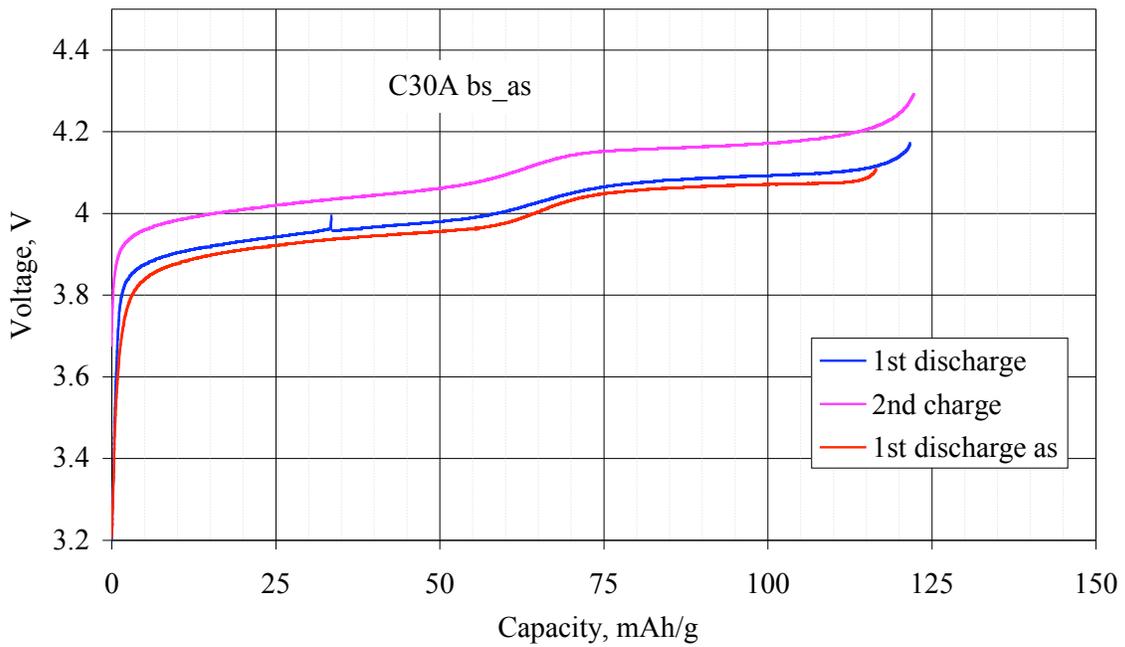


Figure 14 Charge/discharge curves of SM-LMO (30 mM PDDA) -based cathode before and after storage

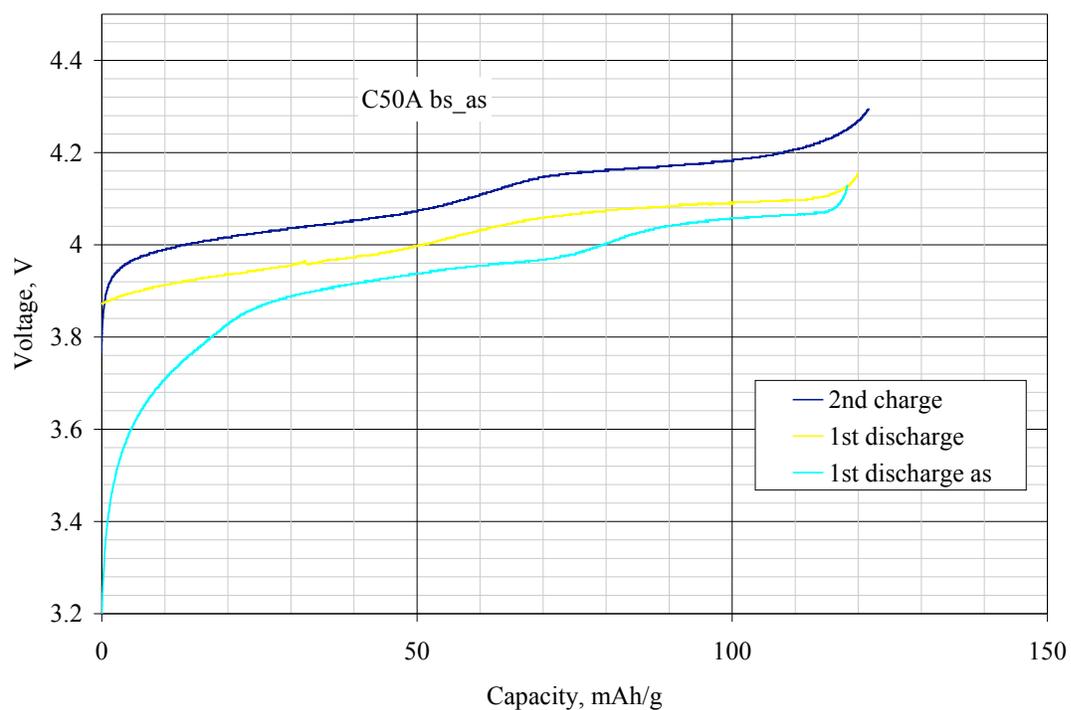


Figure 15 Charge/discharge curves of SM-LMO (50 mM PDDA) -based cathode before and after storage

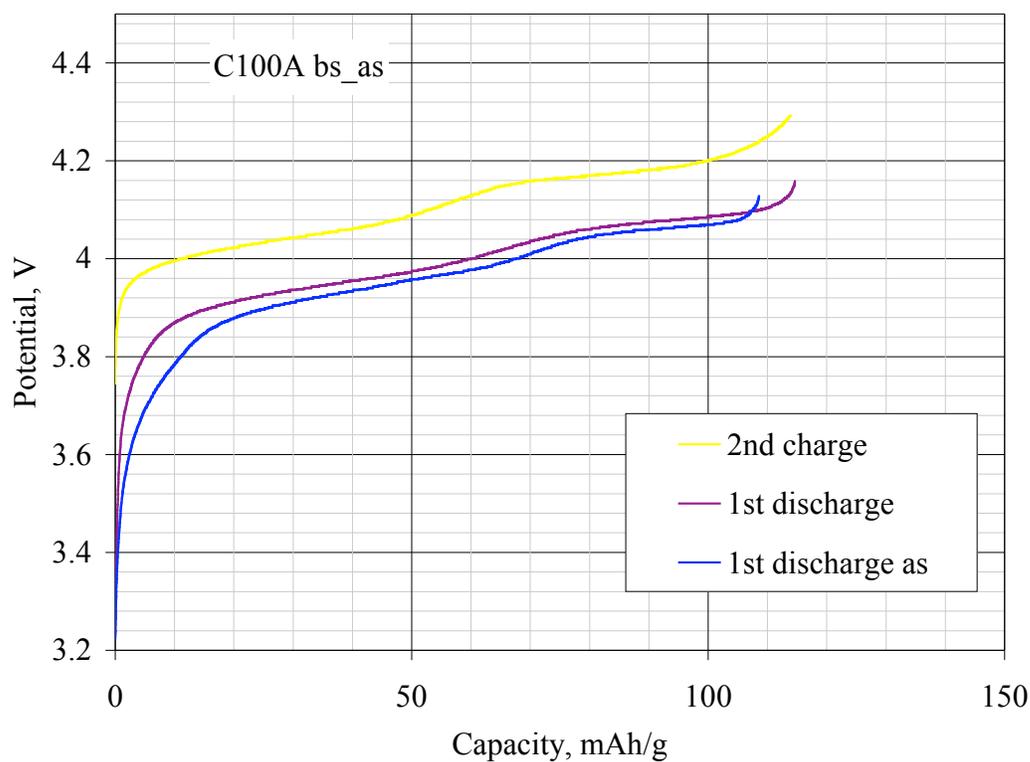


Figure 16 Charge/discharge curves of SM-LMO (100 mM PDDA) -based cathode before and after storage

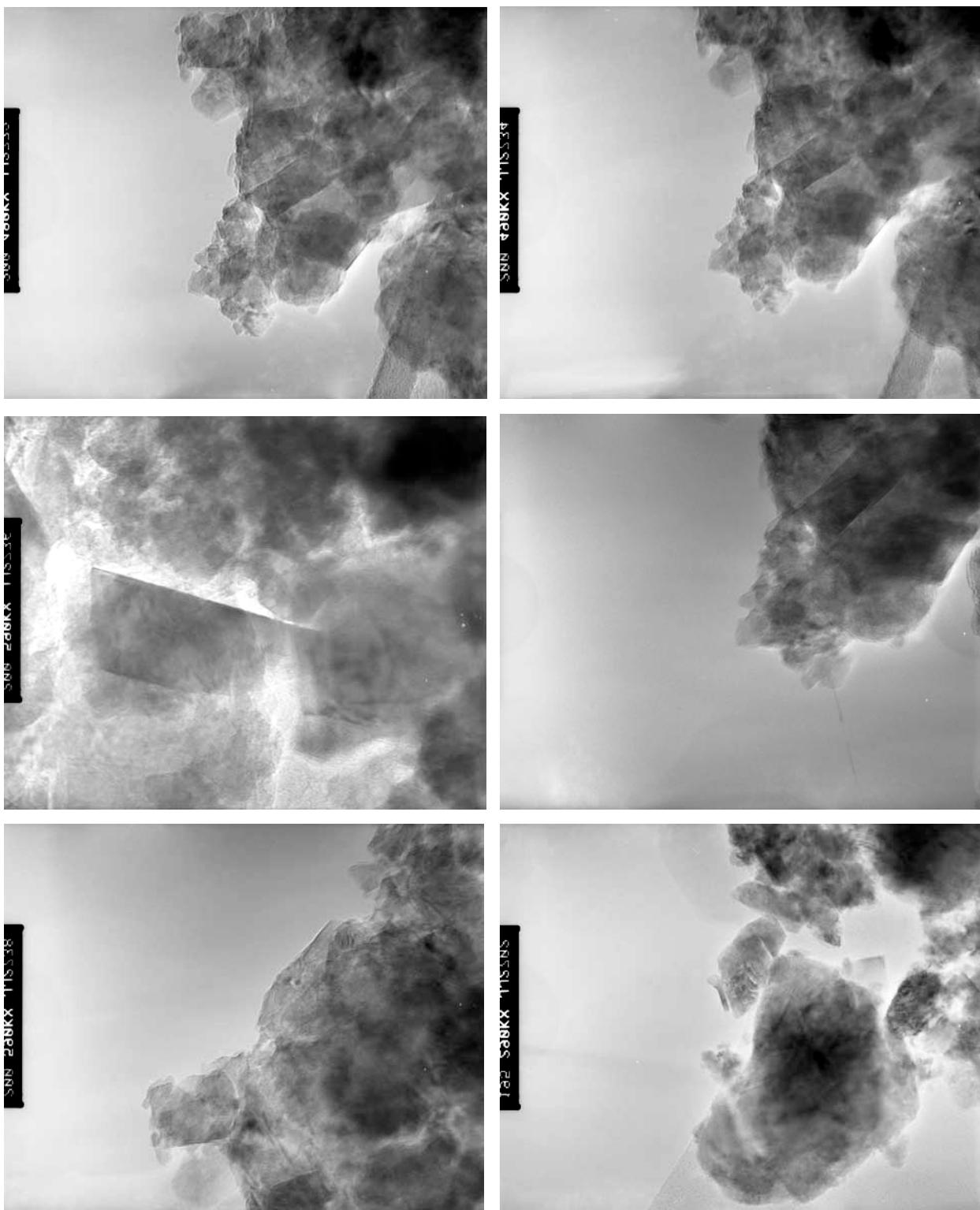


Figure 17 TEM images of SM-LMO (30 mM PDDA) powder. The powder has been prepared for TEM observation by grinding in methanol

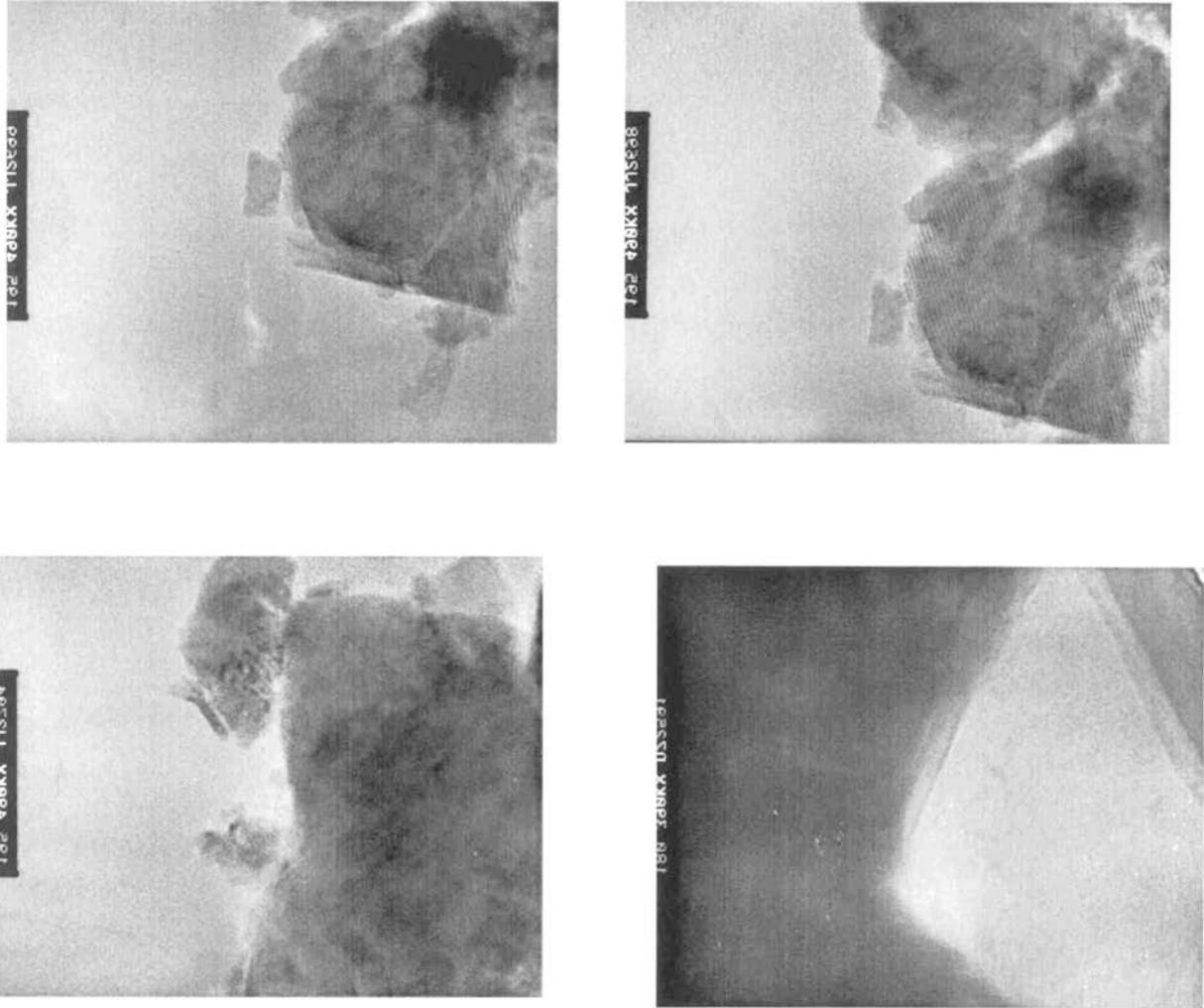


Figure 18 TEM images of SM-LMO (30 mM PDDA) powder. The powder has been prepared for TEM observation by grinding in methanol

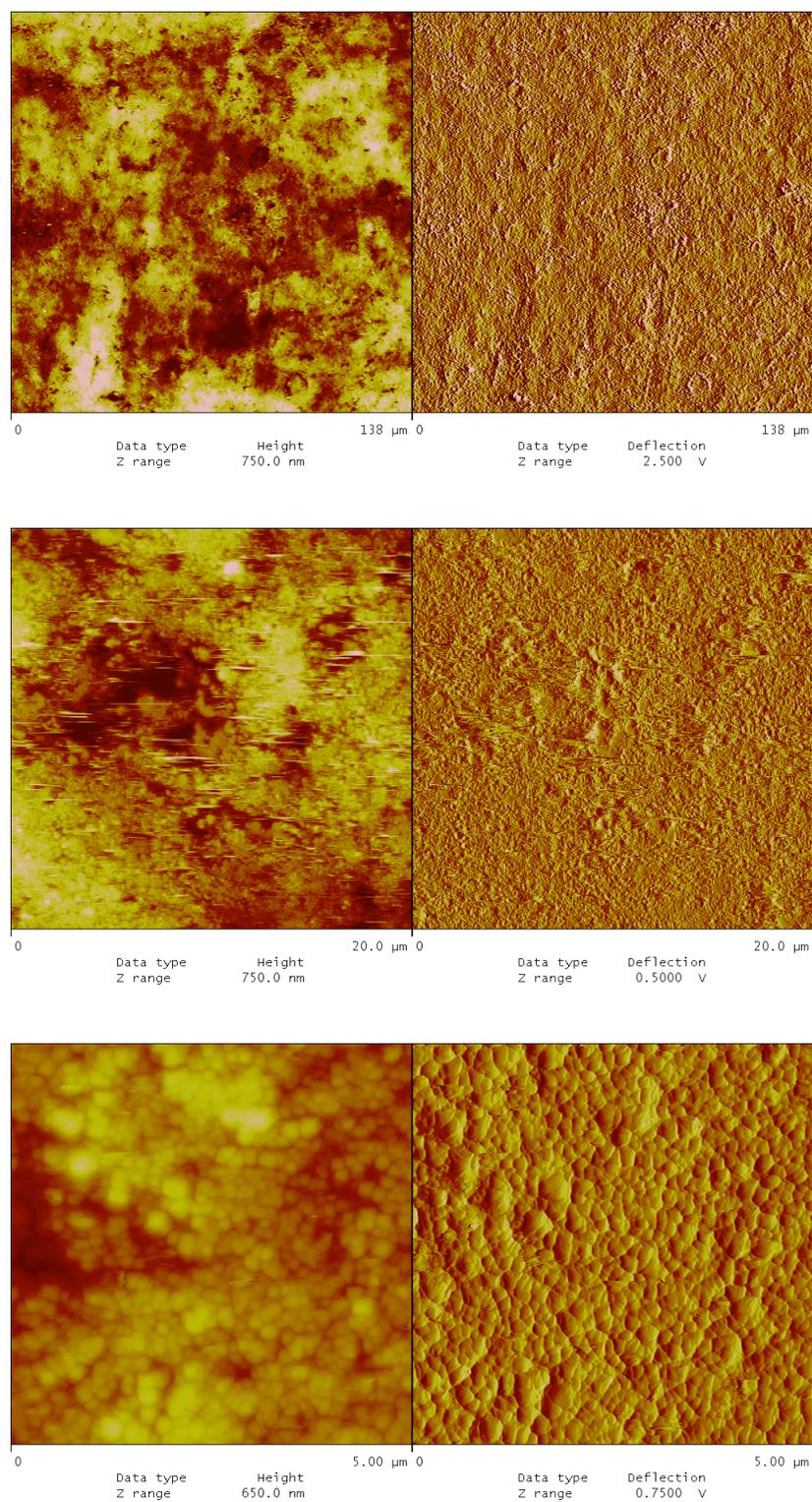


Figure 19 AFM in air in high mode (left) and force mode (right) of cathode surface in air, at different scan sizes. Samples were obtained from PDDA coated LMO powder (in solution containing 30 mM PDDA).

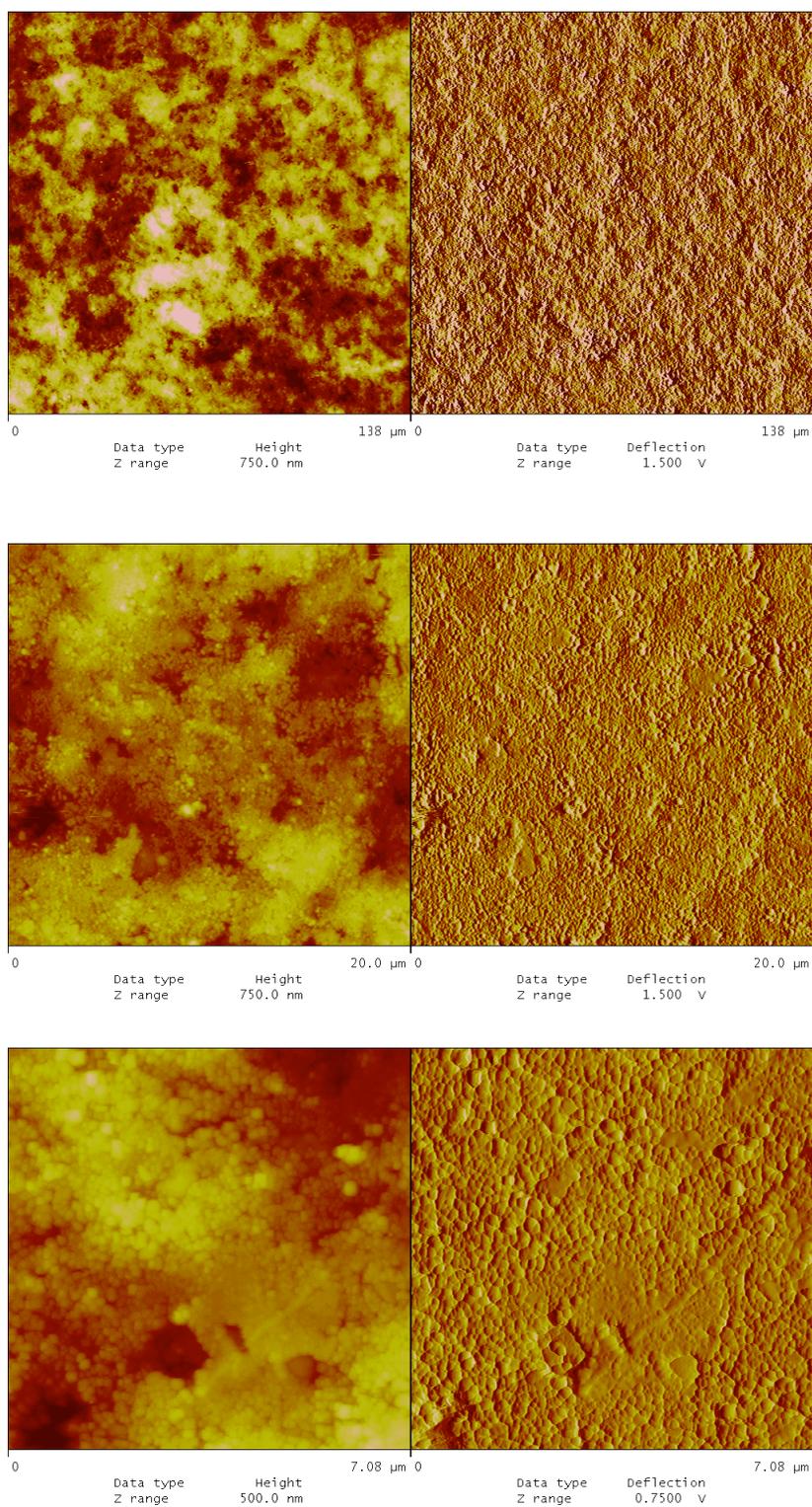


Figure 20 AFM in air in high mode (left) and force mode (right) of cathode surface in air, at different scan sizes. Samples were obtained from PDDA coated LMO powder (in solution containing 100 mM PDDA).

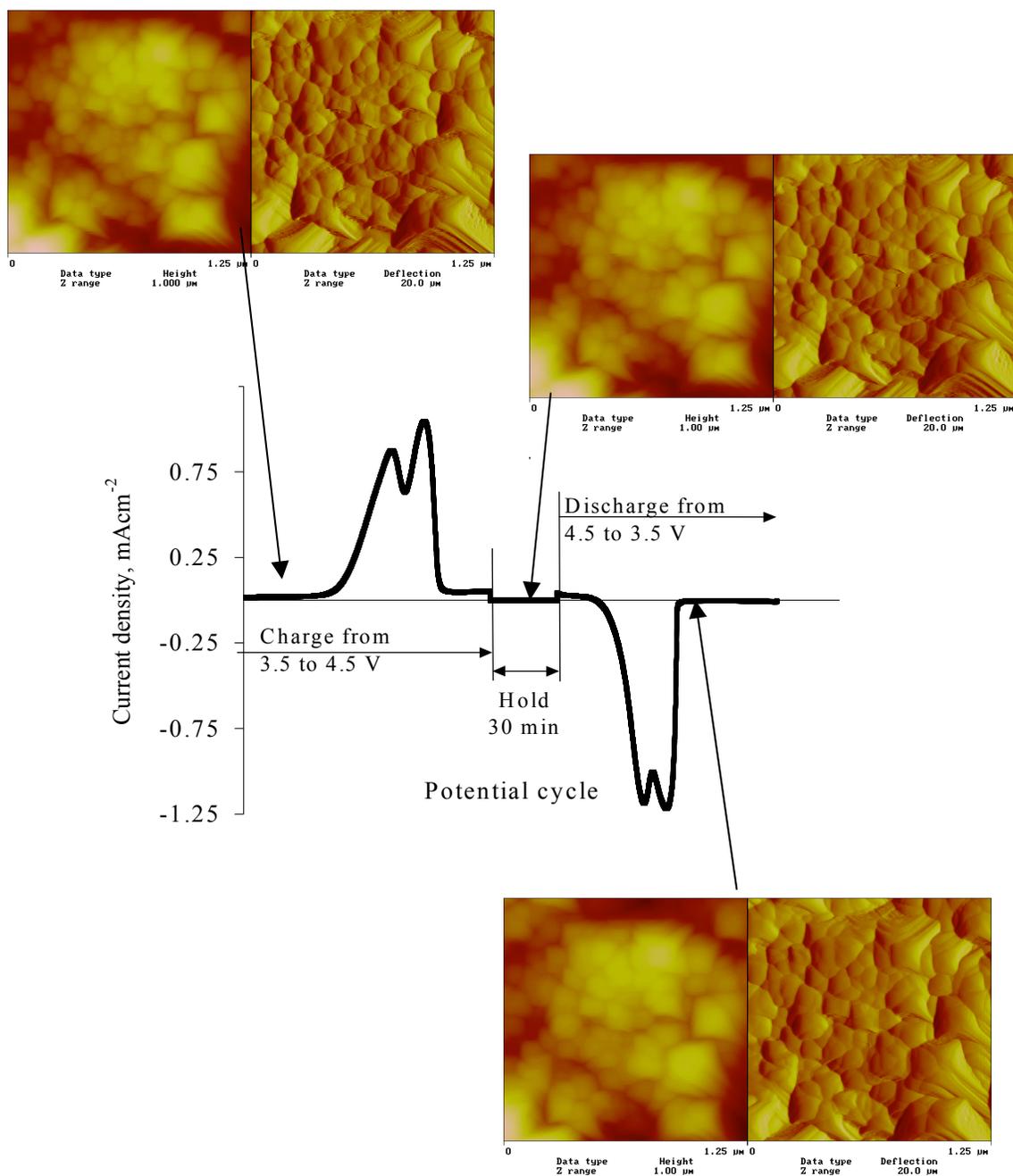


Figure 21 *In situ* EC-AFM of SM-LMO based cathode (30 mM PDDA solution) in 1 M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at room temperature.

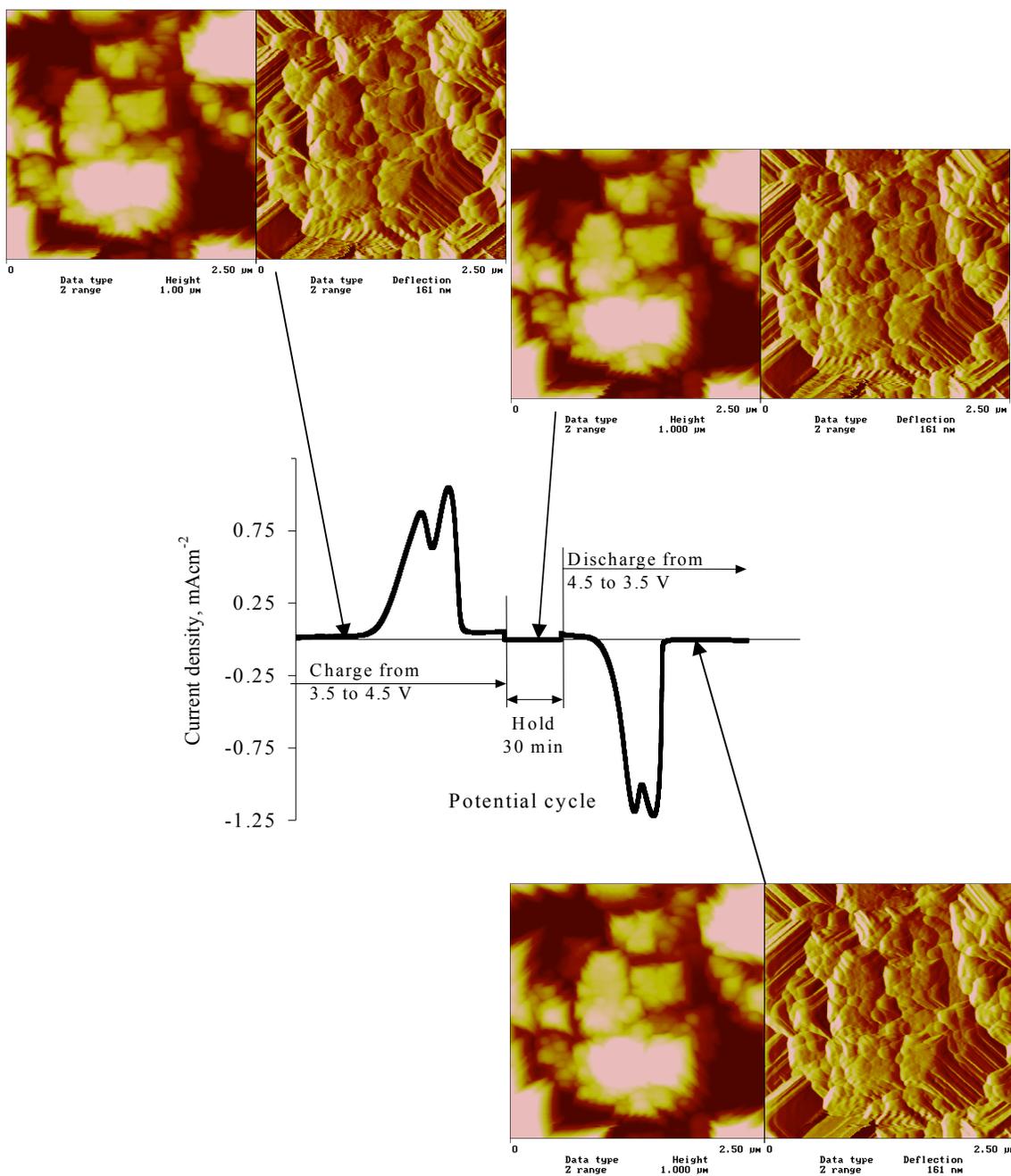


Figure 22 *In situ* EC-AFM of SM-LMO based cathode (30 mM PDDA solution) in 1 M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at elevated temperature (55 °C).

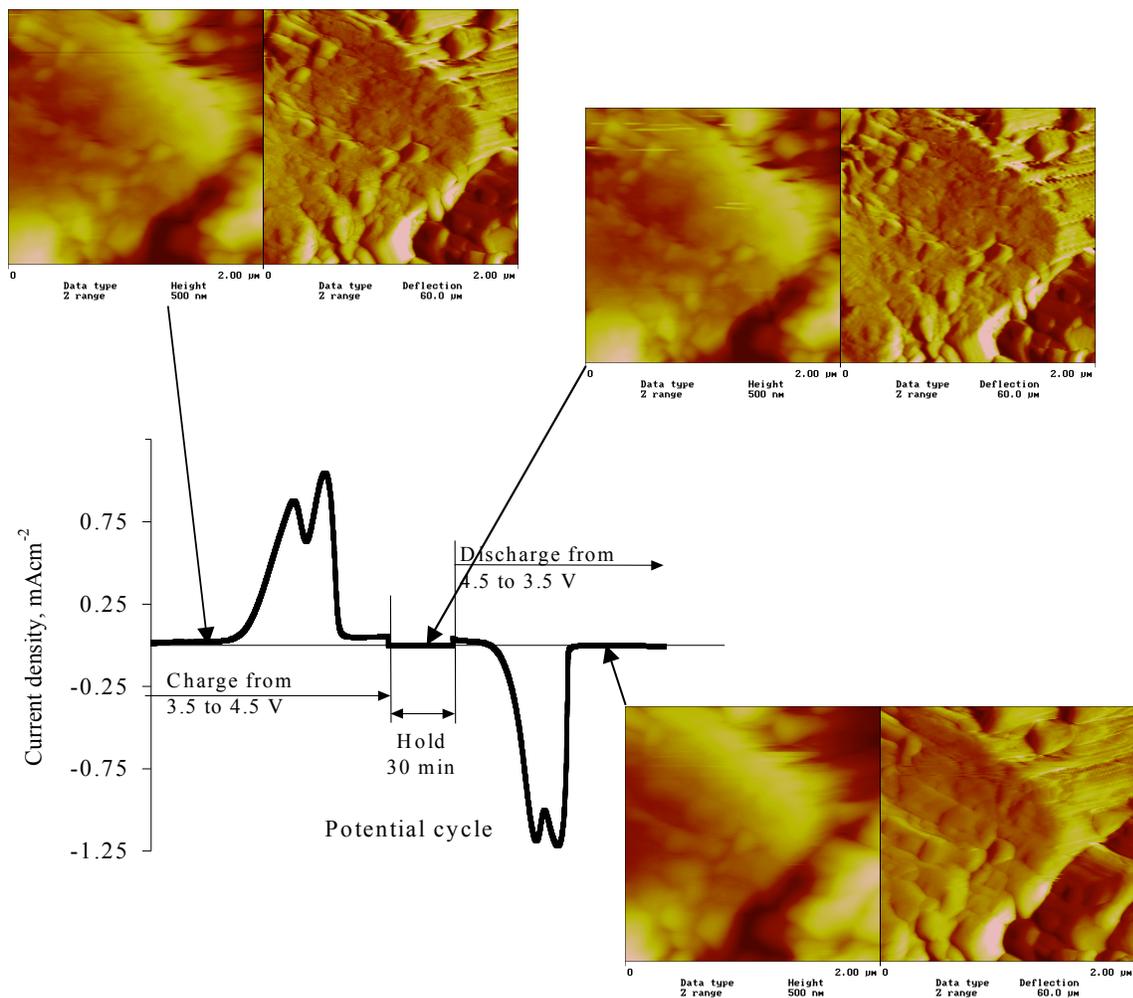


Figure 23 *In situ* EC-AFM of SM-LMO based cathode (100 mM PDDA solution) in 1 M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at room temperature.

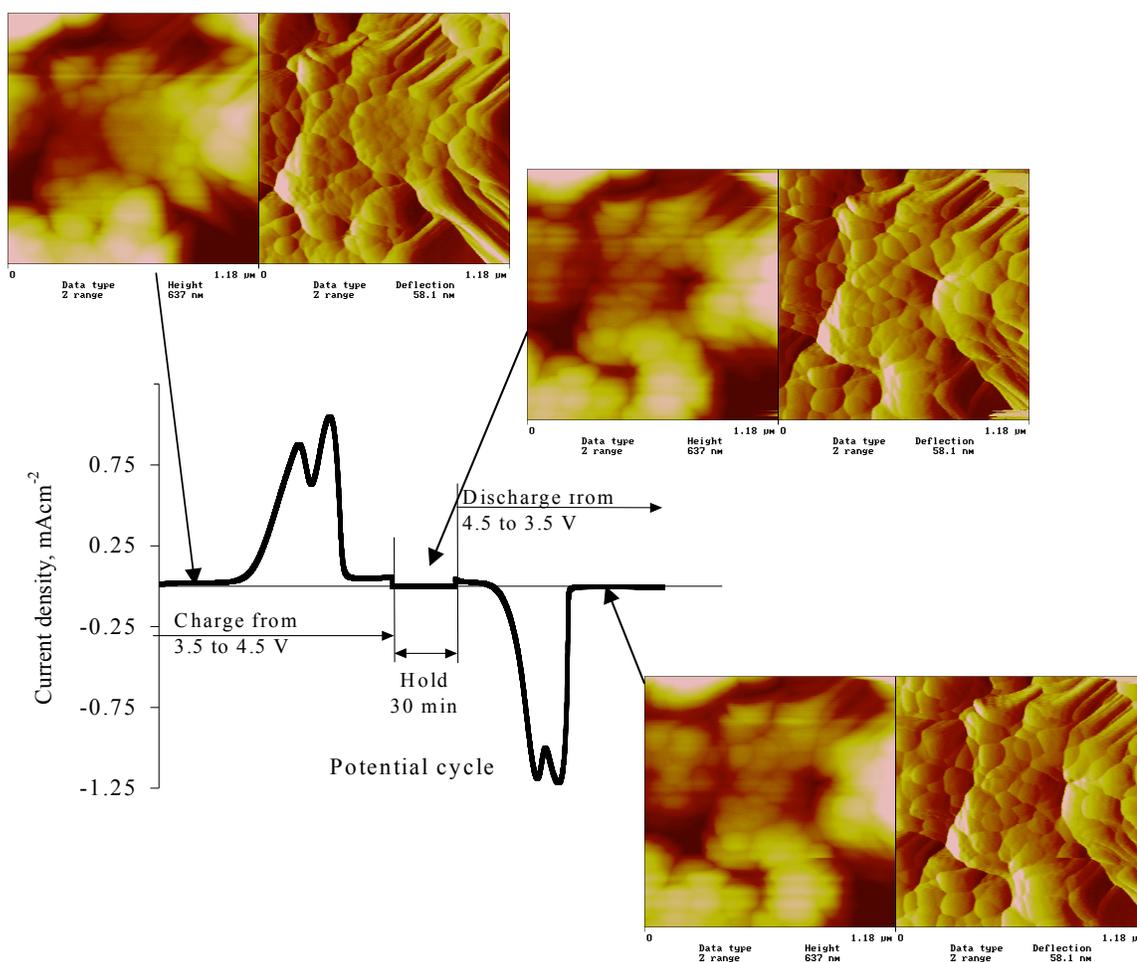


Figure 24 *In situ* EC-AFM of SM-LMO based cathode (100 mM PDDA solution) in 1 M LiPF₆ + EC/DEC electrolyte during charging from E = 3.5 V to E = 4.5 V, holding at 4.5 V for 1/2 h and discharging back to E = 3.5 V, at elevated temperature (55 °C).

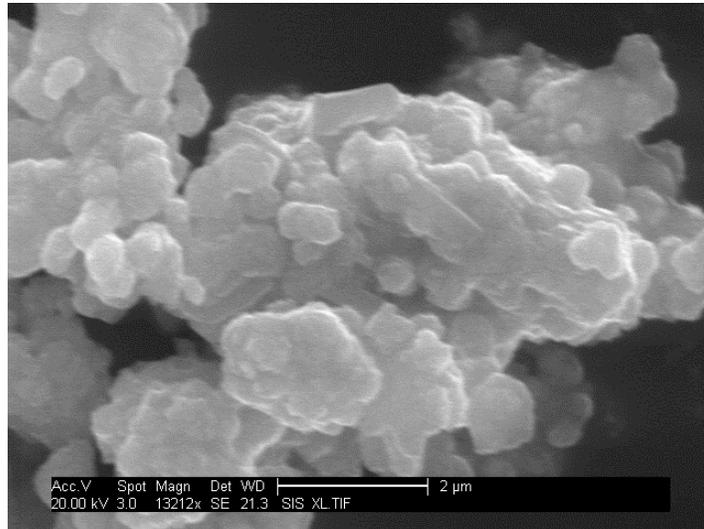


Figure 25 SEM image of LMO powder (before coating)

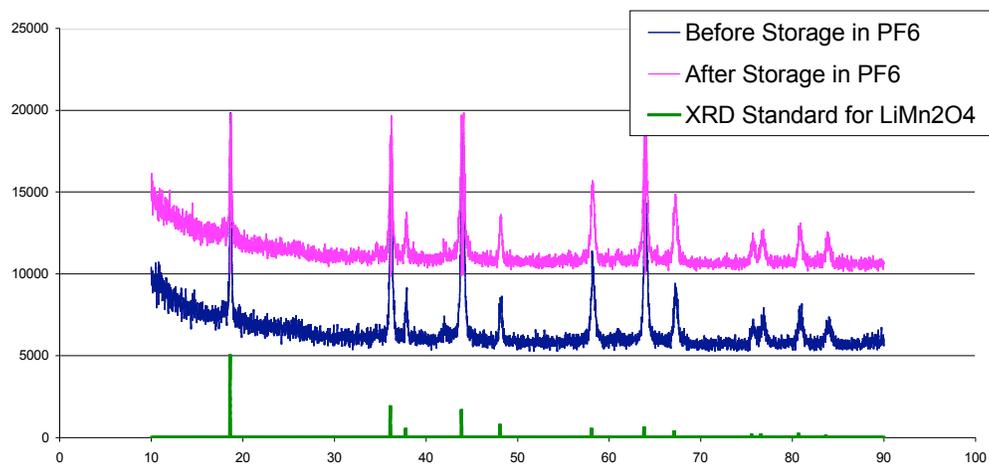


Figure 26 EDAX analysis of LMO –based cathode before and after storage

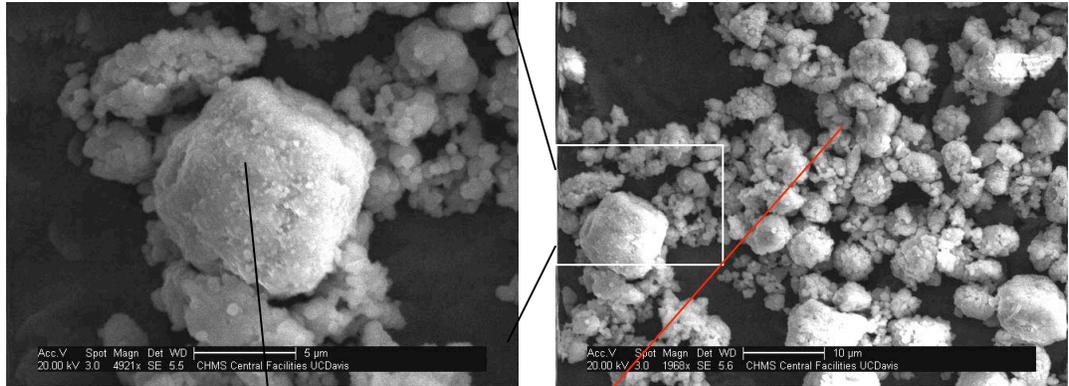
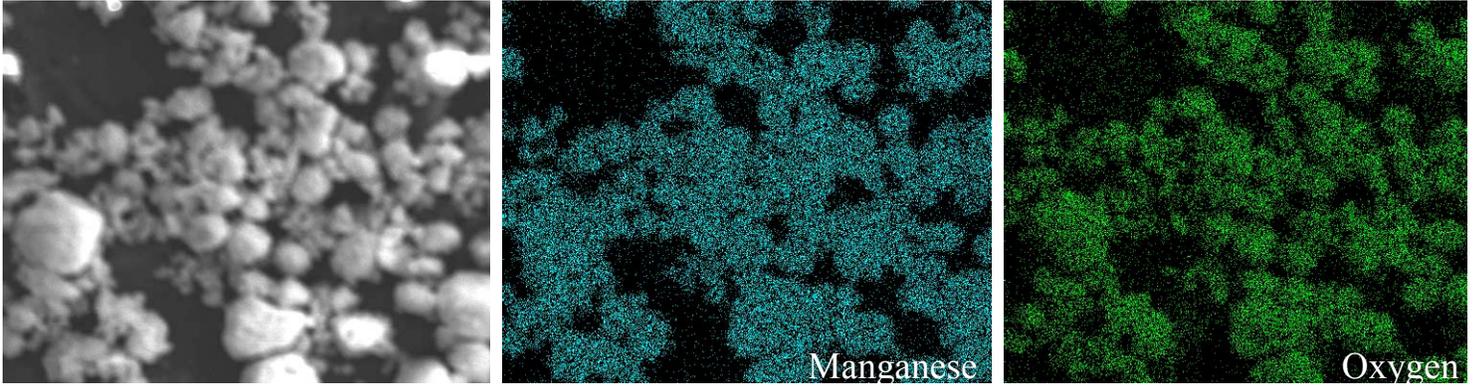
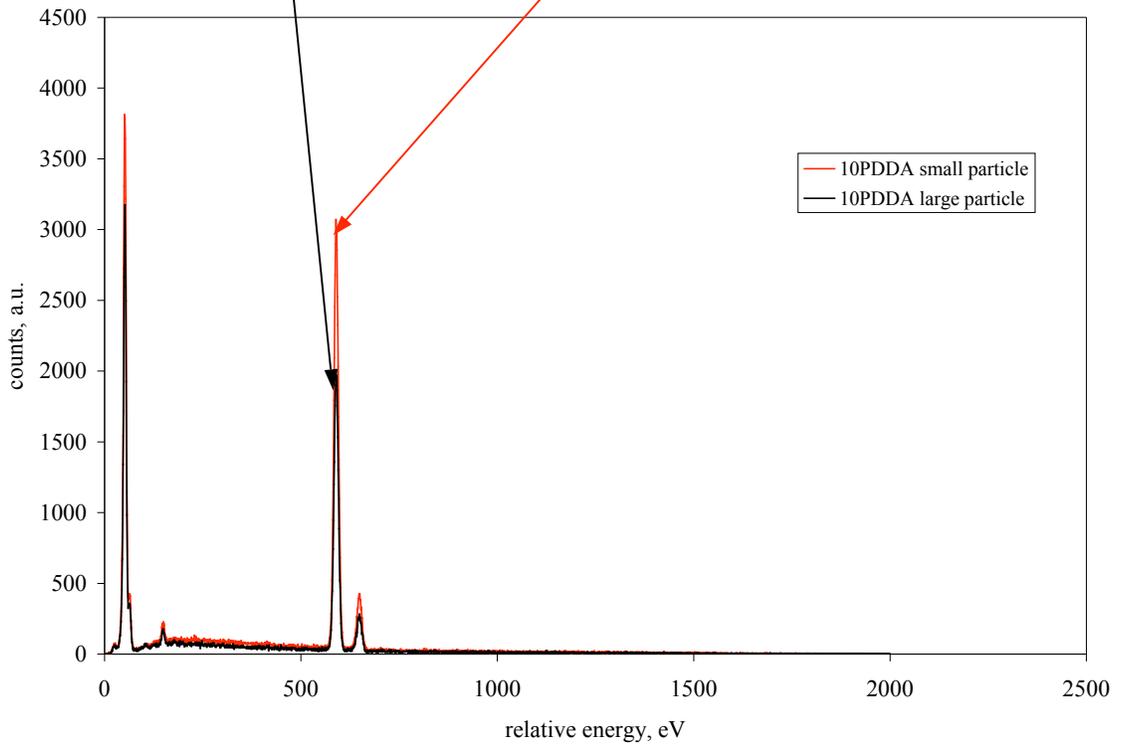


Figure 27 SEM images, elemental mapping and EDAX analysis for PDDA coated powder (in 10 mM PDPA solution).



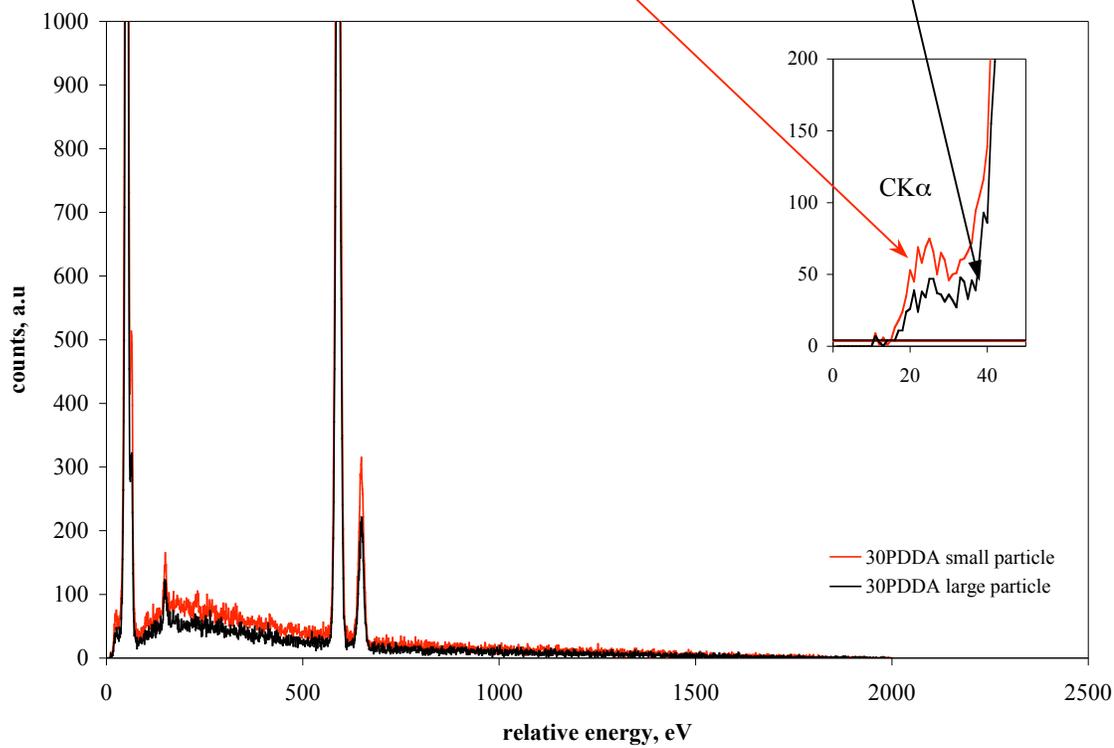
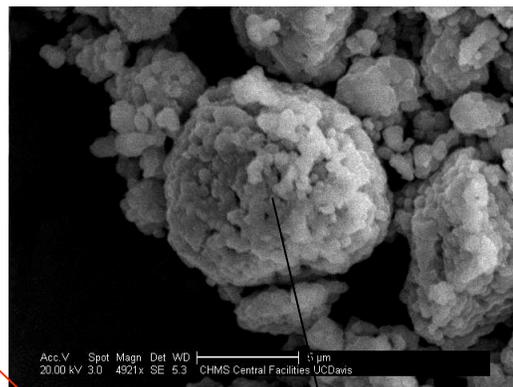
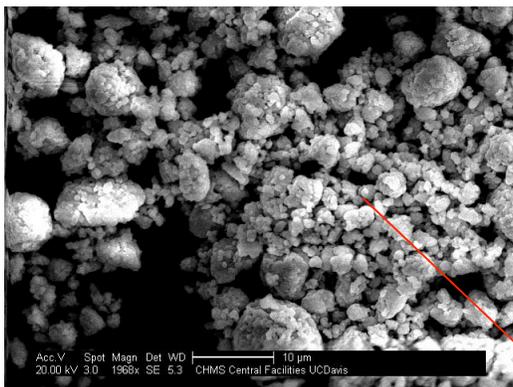
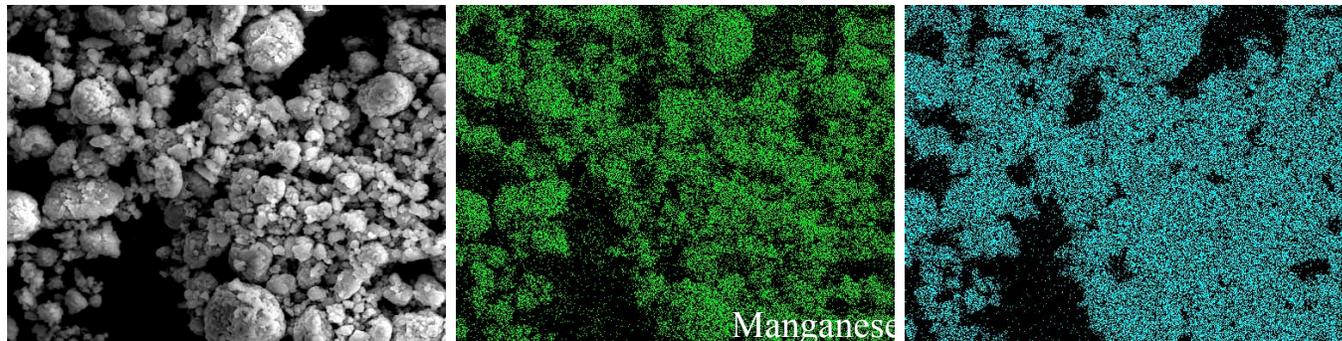


Figure 28 SEM images, elemental mapping and EDAX analysis for PDPA coated powder (in 30 mM PDPA solution).

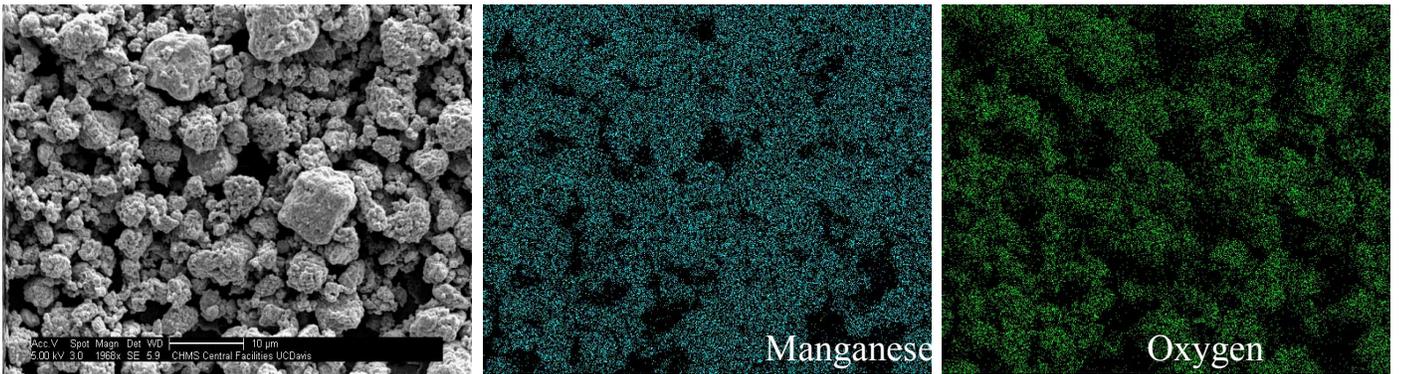
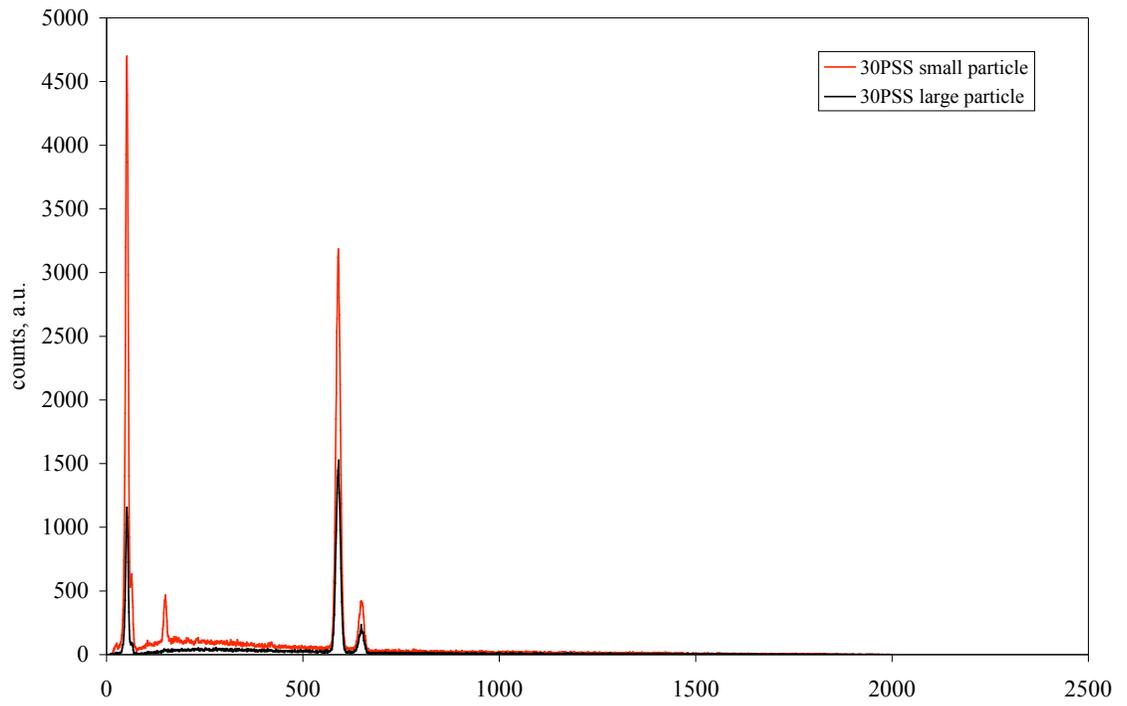


Figure 29 SEM images, elemental mapping and EDAX analysis for PSS coated powder (in 30 mM PSS solution).

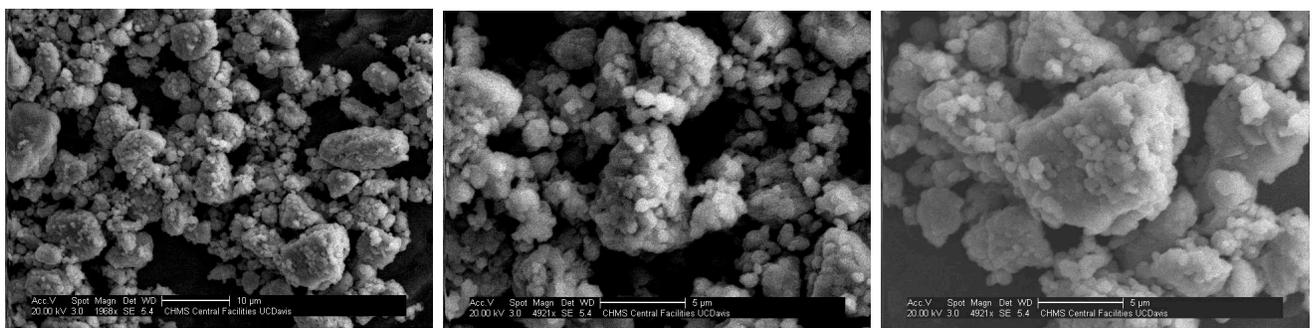
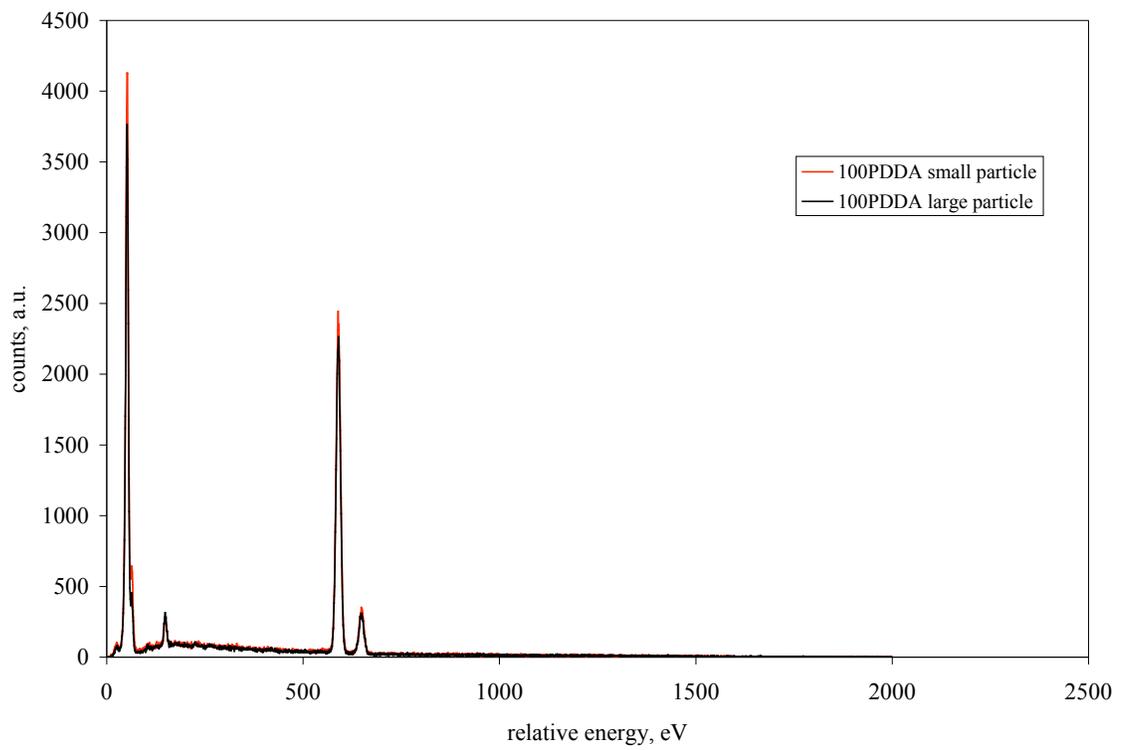
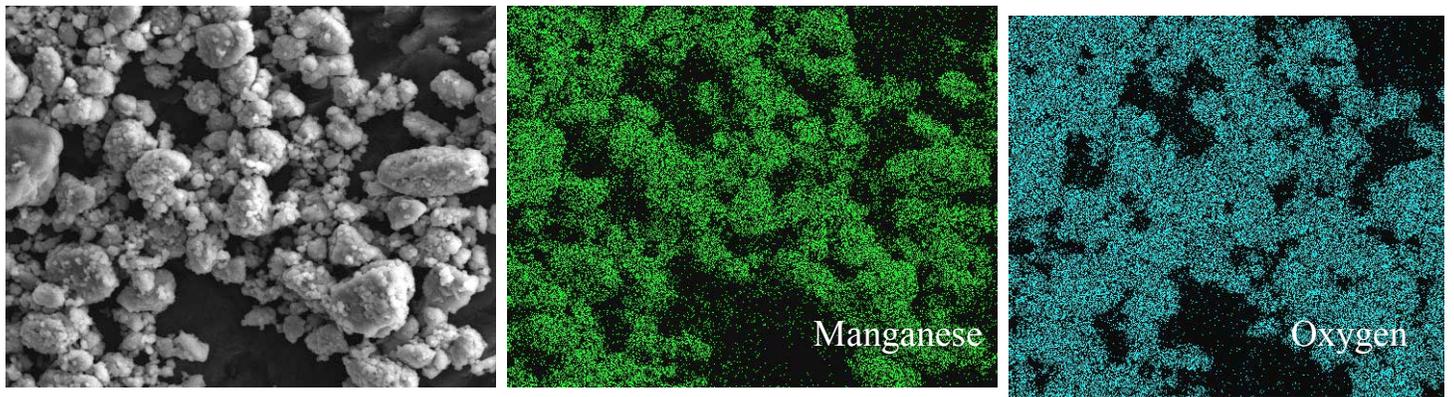


Figure 30 SEM images, elemental mapping and EDAX analysis for PDDA coated powder (in 100 mM PDDA solution).

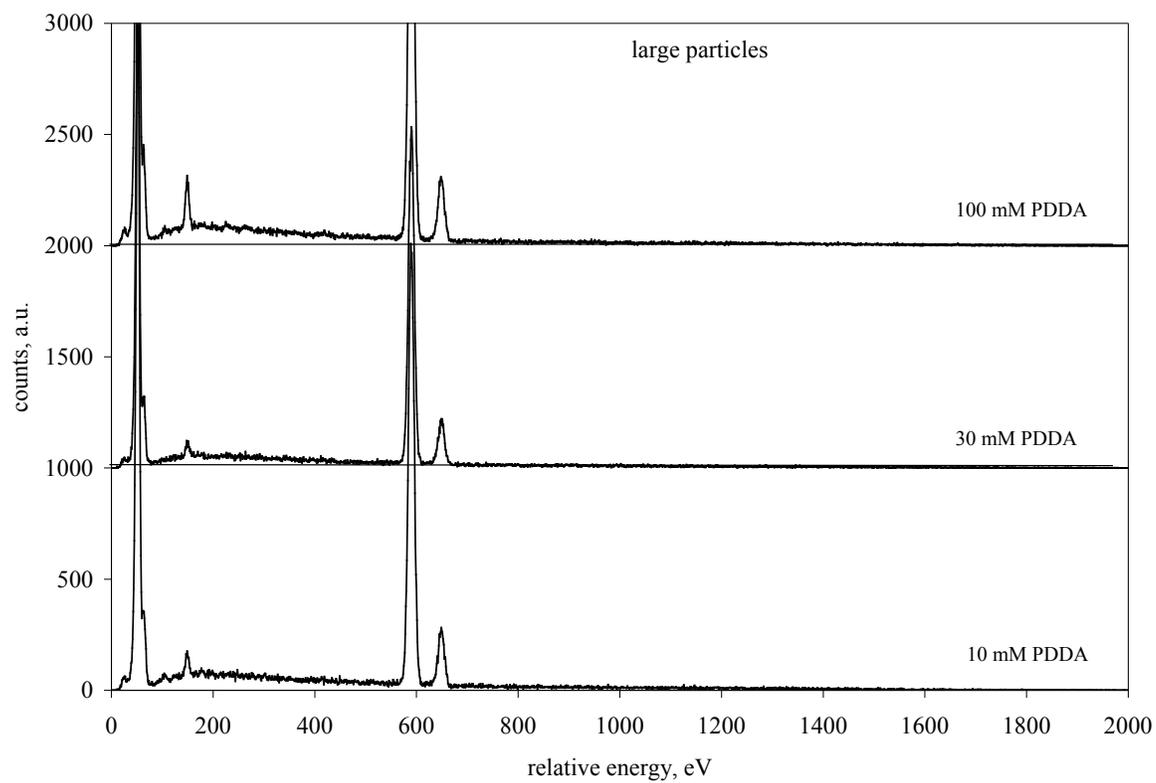
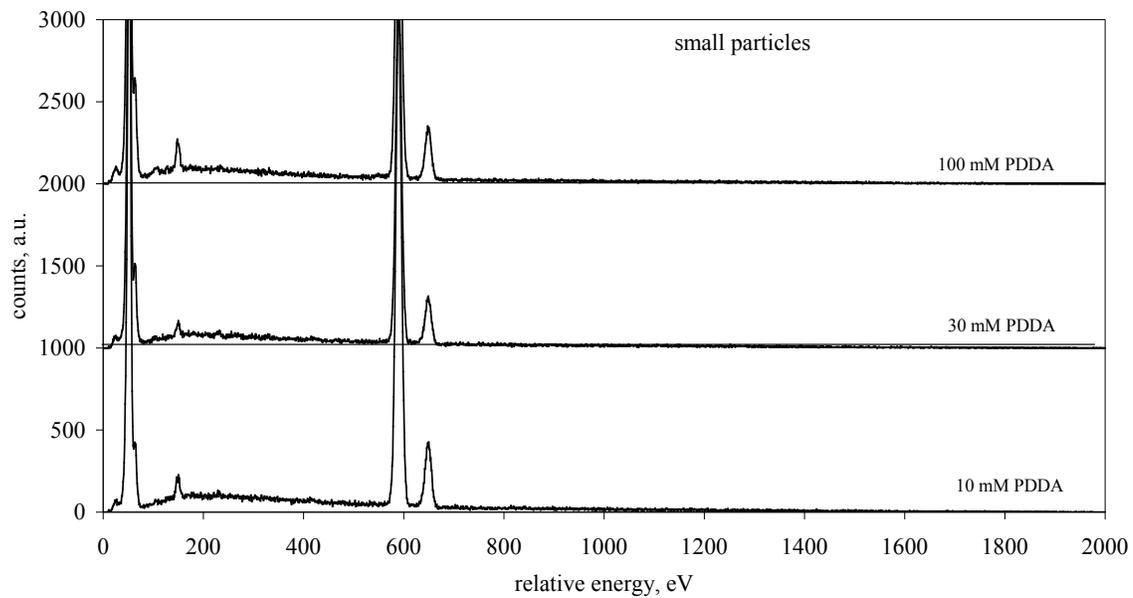
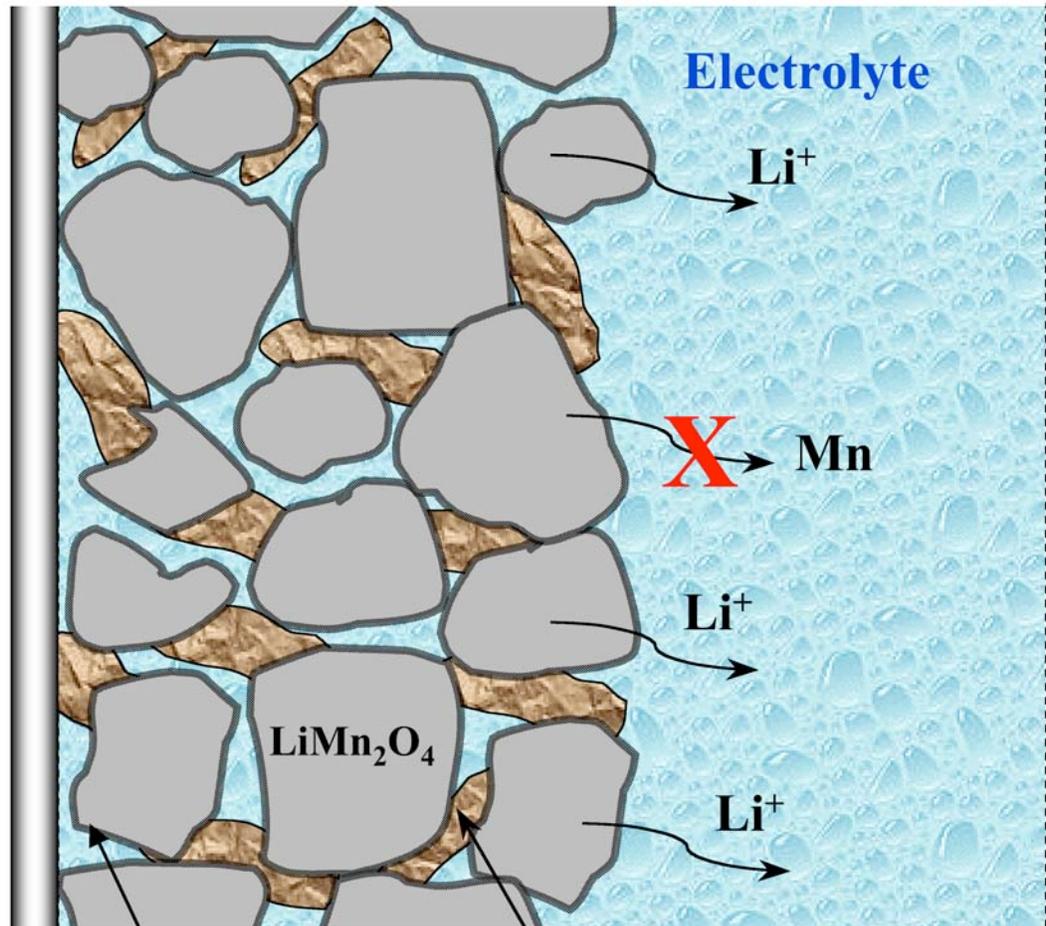


Figure 31 Comparison of EDAX data for large and small particles

Appendix I

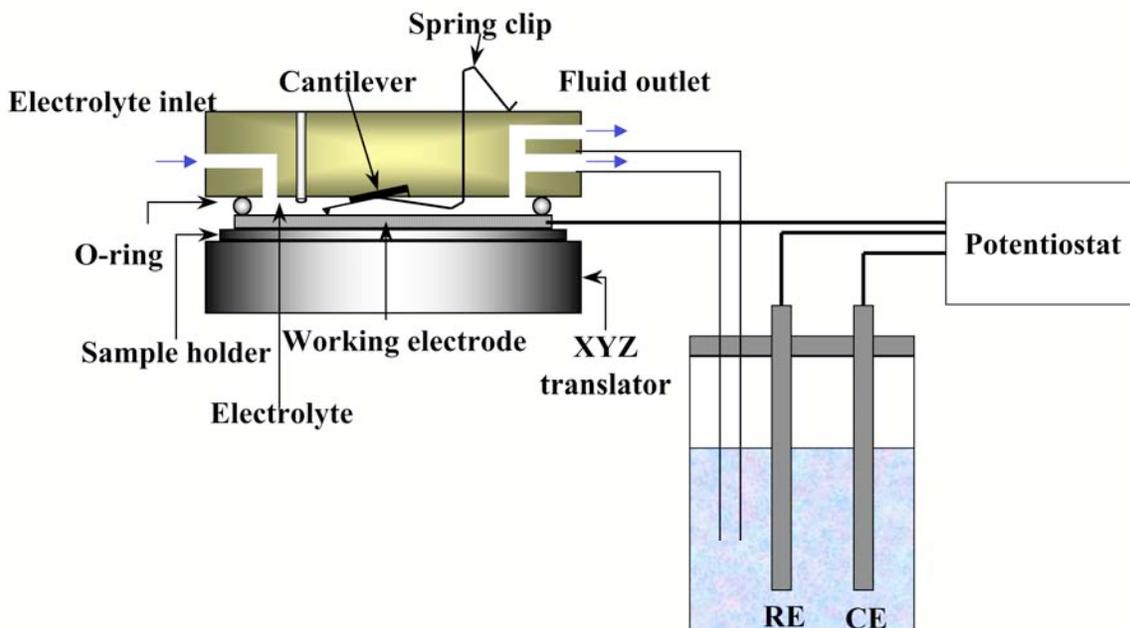


PVDF and carbon black

Ultrathin polymer film
• transport of Li^+ but block Mn ion

Surface Modified LiMn_2O_4 -based Cathode

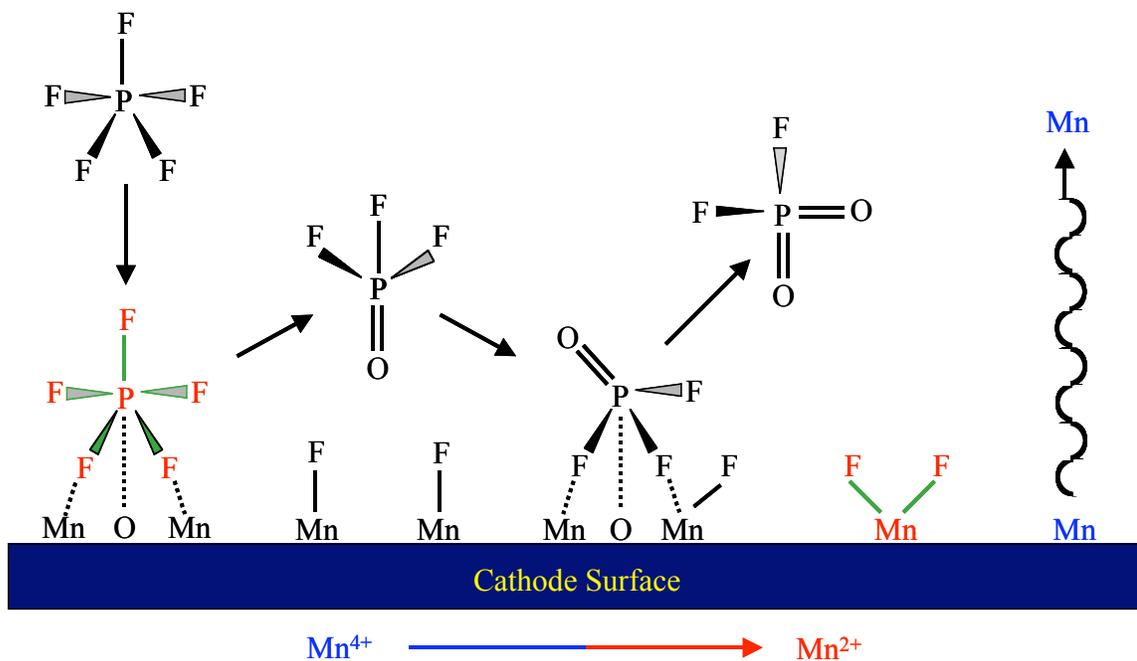
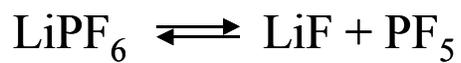
Appendix II



Electrochemical atomic force microscopy (EC-AFM) cell set-up for studying the cathode surface under applied potential

The *in situ* electrochemical atomic force microscopy observation of the cathode surface will be performed using a Multimode AFM (NanoScope IIIA, Digital Instruments). The imaging techniques include *in situ* contact mode, *in situ* electrochemical lateral force microscopy (EC-LFM) and *in situ* tapping mode (TM-AFM) in an organic electrolyte in order to maximize the information about the cathode surface under various potential/temperature conditions. The electrochemical cell used in EC-AFM is similar to the cell used for other electrochemical measurements, e.g. it consists of cathode material as the working electrode and two lithium sheets as counter and reference electrodes. Active electrochemical control and simultaneous observations of the surface reactions will be carried out in the AFM set-up. The applied potential/current will be monitored through a bipotentiostat conductive tape. The electrochemical cell consists of glass and is placed over the sample. An O-ring seals the electrolyte.

Appendix III



Proposed Mechanism of Degradation