Direct Electrodeposition of Thick, Energy Dense Lithium Manganese Oxide Cathodes for Lithium-Ion Batteries

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Presenter: Omar Kazi[1] (omarak2@illinois.edu)
Faculty Mentors: Dr. Paul V. Braun[2,3] and Dr. Minjoo L. Lee[1]
Graduate Mentor: Arghya Patra[2]

[1]Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign
[2]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign
[3]Department of Chemistry, University of Illinois at Urbana-Champaign

[Slide 1]: Introduction

Hello. My name is Omar Kazi, and I am a senior in Electrical Engineering at the University of Illinois at Urbana-Champaign. I am an undergraduate research assistant in Professor Paul Braun's group in the Department of Materials Science and Engineering. Today I will be presenting my research project on the direct electrodeposition of thick, energy-dense lithium manganese oxide cathodes for lithium-ion batteries.

[Slide 2]: Drive Towards Small-Scale Electronic Devices

As we continue to approach the physical limitations of Moore's law, many new small-scale technologies and devices have been innovated using these miniscule transistors and components. For example, microrobots are electronic devices being developed for applications such as environmental and medical sensors. On the left, you can see the "RoBeetle" developed at USC, which is currently the lightest reported microrobot in the world at a weight of 88 mg, which is equivalent to the weight of just 3 grains of rice. The same lab at USC has developed many other small-scale bioinspired microrobots, all of which are extremely lightweight and many of which are battery powered. The image on the right is a microscale aerial robot developed at Harvard which flaps its wings to fly and is powered by a rechargeable battery with a small solar cell. For systems such as these, lithium-ion batteries could be extremely useful, but for such small scales, commercially available batteries are too heavy and can limit the minimum achievable weight, which in turn significantly affect locomotion and aerodynamics.

[Slide 3]: Limiting Factors of Energy Density for Lithium-Ion Batteries

Thus, to make smaller and lighter batteries, we would like to make battery materials with higher volumetric energy densities. Looking at the typical manufacturing process for lithium-ion batteries, we want to minimize or eliminate the use of inactive components in the electrodes to reduce the overall volume and mass. Lithium-ion batteries are commonly synthesized as powders through solid-state reaction and are then slurry-casted onto a substrate using binders and conductive additives. The cathode is then used to make an electrochemical cell, which is packaged into a useful battery. The plot on the right compares the volume and mass distributions

of cathodes made through electrodeposition compared to conventional manufacturing. You can observe that binders and additives take up to 20% of the mass and 40% of the volume of conventional batteries, but we can eliminate these through electrodeposition.

[Slide 4]: Synthesis of Cathodes for Lithium-Ion Batteries

Cathodes for lithium-ion batteries are conventionally synthesized through solid-state reaction techniques. However, these reactions require harsh conditions to be maintained, including high temperatures (above 700 degrees Celsius) and high pressures. This results in the production of very fine crystalline powders which must be slurry casted onto a foil substrate using binders and additives (typically PVDF and carbon black powder). Electrodeposition can alleviate many of these problems, with single-step molten salt synthesis being achievable at more intermediate temperatures (between 250 to 300 degrees Celsius). Electrodeposition does not require high pressure enclaves, nor any binders or additives because the cathode is deposited directly onto the substrate. Therefore, the mass and volume occupied by inactive materials is effectively eliminated. Electrodeposition also allows more control to synthesize thicker cathodes. The thickest electrodeposited LMO cathode reported in literature is about 1 micron thick, although our group has been able to directly grow cathodes 25 microns thick (as shown in this SEM image).

[Slide 5]: Lithium Manganese Oxide (LMO) Cathodes

The most common cathode material used in lithium-ion batteries is lithium cobalt oxide. However, the cathode material of particular interest to us is lithium manganese oxide, which shows a higher thermal stability for high temperature battery applications. In addition, manganese is more abundant, inexpensive, and environmentally benign than cobalt, making it attractive as an alternative material. In literature, LMO cathodes have been synthesized in many different structures and phases through electrodeposition and sputtering techniques. However, the thickness and density of these reported materials is very poor, resulting in a low volumetric energy density. This can be seen clearly through the high porosity of the micron thick nanomesh and nanowire cathodes shown in these SEM images. We would like to be able to deposit highly crystalline and dense (low porosity) cathodes to achieve higher energy densities. This way, we can reduce the size of a battery while maintaining a high power output for microelectronic applications.

[Slide 6]: Electrodeposition of $LiMnO_2$/Li_2MnO_3 Cathodes

Our electrodeposition synthesis process occurs in a three-electrode system using a molten salt bath consisting of an LiOH/KOH eutectic with a manganese oxide (Mn_3O_4) precursor. The working and counter electrodes are both nickel foils, with the counter electrode being larger in area to ensure complete coverage of the working electrode for ion flow between the two electrodes. A cobalt wire is used as a reference electrode. A pulsed voltage is passed through the electrodes in order to achieve the oxidative synthesis of LMO onto the working electrode. The voltage input is pulsed to eliminate diffusion limitations in ion transport through the electrolyte. The cyclic voltammetry plot shows where the oxidation of Mn^{2+} to Mn^{3+} and the oxidation of Mn^{3+} to Mn^{4+} occur. We select a voltage amplitude of 1.2 V for the process because it is high enough to ensure that both oxidations are able to take place.

[Slide 7]: Phase Characterization of Electrodeposited LMO

Following the electrodeposition process, an x-ray diffraction of the sample shows a phase composition of 77% orthorhombic LiMnO2 and 23% Li_2MnO_3. This sample is then annealed at 550 degrees Celsius for 6 hours, resulting in a more balanced phase distribution of 45% orthorhombic $LiMnO_2$ and 55% Li_2MnO_3. The annealing process improves the capacity of the cathode, as the Li_2MnO_3 phase has a higher theoretical capacity than that of $LiMnO_2$.

[Slide 8]: First Demonstration of >20 µm Thick, Energy-Dense LMO

Through this electroplating method, we were able to achieve the first demonstration of LMO greater than 20 microns thick being directly synthesized in a single-step electrodeposition. We can do so at a high growth rate of 11.36 microns per hour (so it takes about two hours to complete the electroplating process). In addition, the material is over 98% dense; far less porous than the samples found in literature. In the SEM images, we can clearly observe the Li_2MnO_3 phase (shown in the top SEM image) and the $LiMnO_2$ phase (shown in the bottom SEM image). We can also observe a vertically aligned layered structure with these two phases. Lithium ions are able to diffuse through the narrow parallel linear pores that can be seen along the $LiMnO_2$ crystalline structure.

[Slide 9]: Electrochemical Performance of LMO

Next, we tested our electrodeposited cathode by constructing a battery using a lithium foil anode and a $LiPF_6$ electrolyte in a CR2025 coin cell. The electrochemical performance of this cell is characterized through galvanostatic potential cycling with potential limitations. Our results show an energy density of 303.1 Wh/kg for the LMO cathode prior to annealing, and 329.4 Wh/kg after annealing. The increase in energy density can be attributed to the more crystalline structure as well as the shift in phase composition to make the material richer in Li2MnO3. The blue curve in the plot on the left represents the cathode after annealing, and we can more clearly observe the voltage plateaus which arise from the crystallized structure.

In the plot on the right, we can see how the areal capacity changes as the battery goes through several charge/discharge cycles, with the capacity remaining fairly stable across 25 cycles with a high coulombic efficiency (above 95%). The average areal capacity across 25 cycles is approximately 1.5 mAh/cm^2. This shows an improvement over the capacities reported in literature for LMO synthesized through sputtering, which ranged from 0.15 to 1 mAh/cm^2.

[Slide 10]: Summary

To summarize the results of this project, we are successfully able to electrodeposit LMO as a cathode material for lithium-ion batteries in thick quantities, and our group is the first to demonstrate depositions with thicknesses over 20 micrometers. The phase composition of the electrodeposited LMO can be controlled through post-processing methods such as annealing, while still maintaining process temperatures lower than those used in state-of-the-art solid-state synthesis techniques. The material which we deposit is over 98% dense, improving its areal capacity and energy density metrics. This makes these cathodes even more useful for small-scale lightweight batteries, such as for the microrobot applications we discussed earlier. The cathode material is also proven to be stable for several usage cycles of charging and discharging.

[Slide 11]: Acknowledgements

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