CHARACTERIZATION OF THE Li-CoO CONVERSION REACTION USING ANGLE-RESOLVED X-RAY PHOTOELECTRON SPECTROSCOPY (ARXPS)

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Abstract

A proposed alternate mechanism for energy storage in solid-state lithium-ion batteries is the conversion reaction between Li and CoO to form Co$^0$ and Li$_2$O. The goal of this experiment was to characterize the phase front of this conversion reaction using angle-resolved x-ray photoelectron spectroscopy (ARXPS). The conversion reaction was induced by lithiating epitaxial CoO(100) grown on a Ag(100) substrate. ARXPS analysis suggests that a surface layer of Li$_2$O$_2$ formed atop a heterogeneous layer of Co$^0$ and Li$_2$O, which formed above remaining unreacted CoO.
**Introduction**

As modern technology grows in power consumption and sophistication, so too does the need for improvements in energy sources. Lithium-ion batteries are popular primary sources of energy for wireless devices, and their widespread use makes them an important technology for further development. One area of scientific inquiry regarding these batteries is the possibility of using alternative energy storage mechanisms with different electrode materials to improve their charge densities.

**Lithium Intercalation Batteries**

The traditional design of a lithium-ion battery relies on a process of intercalation. This is a process in which $\text{Li}^+$ moves out of a porous carbon anode material, passes through electrolyte solution in the cell and inserts itself into a porous cathode material, usually $\text{CoO}_2$, during discharge. It does so according to

$$x\text{Li}^+ + xe^- + \text{Li}_{1-x}\text{CoO}_2 \rightarrow \text{LiCoO}_2.$$  

![Figure 1: Representation of the Li-intercalation process.](image)

Intercalation batteries have the benefit of high cycling capacity – they may be charged and discharged for 1000’s of cycles [1]. One limiting factor of their capabilities is the mechanism of current production. Each formula unit in the intercalation process can produce a theoretical
maximum of one electron, a limit that puts a constraint on the charge density of these batteries. Li-intercalation batteries have charge densities of approximately 145 mAh/g [1]. This fundamental limit and recent advancements in nanophysics have motivated research into an alternative mechanism of energy storage.

Conversion Batteries

In recent years, it was found that batteries with certain transition metal oxides or fluorides as cathodes exhibited high charge densities and reversibility in storage of Li in reactions called conversion reactions [2]. In these conversion reactions, Li reduces the cathode metal oxide to its metallic form in 2-5 nm grains dispersed in amorphous Li$_2$O according to:

$$\text{CoO} + 2\text{Li}^+ + \text{2e}^- \leftrightarrow \text{Li}_2\text{O} + \text{Co}$$

$$2\text{Li} \leftrightarrow 2\text{Li}^+ + 2\text{e}^-$$

$$\text{CoO} + 2\text{Li} \leftrightarrow \text{Li}_2\text{O} + \text{Co}$$

*Figure 2: Representation of the Li-CoO conversion reaction.*

Use of CoO has been shown to have potential as the cathode material in a conversion reaction. In capacity and cycling studies of various transition metal oxides, it was found that not only does the charge density of batteries using this material exceed that of conventional
intercalation batteries (715 mAh/g, compared to 145 mAh/g) but also that its reversible capacity remained constant over multiple cycles [1][2]. The reversibility of conversion reactions is constrained by the decomposition of the formed Li$_2$O matrix. Bulk Li$_2$O is known to be electrochemically inert, making the reverse reaction thermodynamically unfavorable. When present in a nanoscale matrix, however, a greater proportion of molecules are found in surface regions with respect to the overall volume of the layer, and decomposition of Li$_2$O is more thermodynamically feasible [2].

While the possibility of conversion batteries using CoO is attractive and has garnered scientific interest, there are many aspects of the reaction that remain unknown. To explore the possibility of using the conversion reaction successfully in real batteries, various aspects of the reaction need to be understood. In particular, the phase progressions of the Li$_2$O matrix and Li$_2$O/Co interface of the CoO cathode material is not well-characterized, but can be studied with thin-film analysis.

Two hypothetical morphologies proposed by Maier *et al* are shown in Figure 3.

![Figure 3: Hypothetical morphologies of the Li-CoO conversion reaction.](image)

The first model proposes that lithium diffuses down to the substrate and reacts to form an amorphous mixture of Li$_2$O, metallic cobalt nanoparticles, and CoO. The second model proposes a reaction wherein Li$_2$O and Co nanoparticles exist in a surface overlayer with unreacted CoO below [1]. Given the nanoscale nature of these reactions, and the need for chemical sensitivity
and sub-nanometer depth resolution, angle-resolved x-ray photoelectron spectroscopy (ARXPS) is appropriate for understanding the Li-CoO conversion reaction.

(AR)XPS

X-ray photoelectron spectroscopy (XPS) is a widely-used technique used for elemental and chemical analysis in surface science. XPS is a technique in which the surface layers of samples are irradiated with monoenergetic x-rays, ejecting core-level electrons for analysis of their binding energies. A schematic representation of XPS is represented in Figure 4.

![Figure 4: A diagram of the x-ray photoelectron spectroscopy process.](image)

Using the energy of incident photons ($h\nu$), the kinetic energy ($E_K$) of emitted photoelectrons, and the work function ($\phi$) of the material, all of which are well-known or measurable quantities, the initial binding energy ($E_B$) of detected photoelectrons can be calculated according to

$$ (1) \ E_B = h\nu - E_K - \phi. $$
XPS is an ideal method for characterization of thin films because it can provide quantitative information regarding both sample stoichiometry and chemical bonding. It can provide chemical information because it is sensitive to different oxidation states of the same element being studied. This is because core-level electrons which are probed have different binding energies due to the differences in the electrostatic potentials of atoms in different oxidation states [6].

Angle-resolved x-ray photoelectron spectroscopy (ARXPS) is a modality of XPS in which the angle of detected photoelectrons is varied to enhance the signal from surface layers. XPS has a limited probe depth of 1-5 nm due to the attenuation of photoelectrons through various materials [6]. The electron attenuation length (EAL) is a quantity directly related to the inelastic mean-free-path of core-level electrons passing through materials. Because electron attenuation allows for a fixed depth of analysis, when a sample is tilted and the angle of the detected photoelectron increases with respect to the surface normal, the proportion of signal received from surface layers increases and the intensity of electrons able to reach the analyzer from deeper layers. An outline of this process is sketched in Figure 5. Using this angle-dependence of the signal, compositional depth profiling of samples can be achieved with proper analysis.

![Diagram](image-url)

*Figure 5: Representation of the variation of signal intensity for different photoelectron detection angles*
ARXPS Modeling Theory

ARXPS analysis is done through manipulation of the Beer-Lambert equation

\[ (2) \ I = I_0 e^{-d/\lambda \cos\theta} \]

where \( \theta \) is the angle to the surface normal of the emitted electrons, \( I \) is the signal intensity of electrons from all depths greater than \( d \), \( I_0 \) is the intensity from an infinitely thick, uniform sample of the studied material, and \( \lambda \) is the attenuation length of the photoelectrons in the material [6].

Figure 6 shows a schematic diagram of the idealized case of a thin layer of material A with thickness \( d \) on top of a semi-infinite substrate B.

![Figure 6: Depiction of a continuous overlayer of material A atop thick substrate B](image)

The intensity of the signal of electrons from A can be derived by integrating Equation (2) from a thickness of 0 to \( d \)

\[ (4) \ I_A = I_A^\infty \left[ 1 - e^{-d/\lambda_{AA} \cos\theta} \right]. \]

\( I_A^\infty \) is the signal one would expect to receive from a semi-infinite sample of material A and \( \lambda_{AA} \) is the attenuation length of electrons from the probed core-level corresponding to material A.
passing through material A. We then consider the signal one would expect from a semi-infinite sample of B ($I_B^\infty$), arriving at the substrate-overlayer interface and attenuated by passing through material A. In a similar manner of integration, the intensity of the signal of electrons from substrate B is

\[ (5) \quad I_B = I_B^\infty \left[ e^{-d/\lambda_{B,A} \cos \theta} \right]. \]

Using the same convention, $\lambda_{B,A}$ is the attenuation length of electrons from the core-level corresponding to material B passing through material A. The ratio of the signals from A to B is then

\[ (6) \quad \frac{I_A}{I_B} = R = R^\infty \left[ \frac{1-e^{-d/\lambda_{A,A} \cos \theta}}{e^{-d/\lambda_{B,A} \cos \theta}} \right] \]

where $R^\infty$ is the ratio of $I_A^\infty$ to $I_B^\infty$. This ratio is plotted as a function of angle in Figure 7.

In the case of a thick overlayer of high-Z materials, elastic scattering in the overlayer of photoelectrons originating in the substrate layer may give rise to additional substrate signal at glancing angles [4]. As a result, corrected attenuation lengths must be used. The value of $R^\infty$ can be calculated from atomic densities (atoms/unit volume) and electron attenuation lengths of the two materials.
\[ (7) \quad R^\infty = \frac{\sigma_{B,A} \lambda_{B,A}}{\sigma_{B,B} \lambda_{B,B}} \]

where \( \sigma_{x,y} \) represents the number of atoms of \( x \) in material \( y \) per unit volume [6].

The previous concept can be built upon to model alternate sample morphologies such as that depicted in Figure 8.

By considering a sample in which materials A and C are segregated in a layer above substrate B, we can modify the idealized model by assuming material A has a fractional coverage \( \Theta_A \) of the surface and that the remainder \( (1 - \Theta_A) \) is covered by material C. The signal from A can be calculated as

\[ (8) \quad I_A = \Theta_A I_A^\infty \left\{ 1 - e^{\frac{-d}{\lambda_{A,A} \cos \theta}} \right\}. \]

The signal from A is similar to that for a continuous overlayer, but scaled by A’s fractional coverage. The signal from B is composed of electrons from B attenuated through A and electrons attenuated through C. The signal from B through A is expressed in (9).

\[ (9) \quad I_{B,A} = \Theta_A I_B^\infty \left\{ e^{\frac{-d}{\lambda_{B,A} \cos \theta}} \right\} \]

The signal from B through C is expressed in (10).
The total signal from B is the sum of the two components, expressed in (11).

\[
(11) \ I_B = I_B^\infty \left[ (1 - \Theta_A) \left\{ e^{\frac{-d}{e^{\lambda_B \cos \theta}}} \right\} + \Theta_A \left\{ e^{\lambda_{A B} \cos \theta} \right\} \right]
\]

In a similar analysis to the case of a uniform overlayer, the angular dependence of signal ratio can be used for spatial profiling of the materials studied.

\[
(12) \ \frac{I_A}{I_B} = R = R^\infty \left[ \frac{\Theta_A \left\{ 1 - e^{\lambda_{A B} \cos \theta} \right\}}{(1 - \Theta_A) e^{\lambda_{B C} \cos \theta} + \Theta_A e^{\lambda_{A B} \cos \theta}} \right]
\]

We will use these models as a basis for analysis of ARXPS data.

**Experimental Methods**

The experiment was composed of three phases. First, approximately 5 nm of epitaxial CoO(100) film was grown on Ag(100). After ARXPS characterization of the initial film, a conversion reaction was induced by lithiating the sample in the ultra-high vacuum chamber. Last, the phase progression of the Li-CoO conversion reaction was studied by means of ARXPS. Both sets of ARXPS data were collected by varying the angle of photoelectron detection from 0° (surface normal) to 50°, and all x-rays used were from a monochromated Al-Kα source with photon energy 1486.7 eV.

The preparation of each CoO thin film was done in a method consistent with Sebastian *et al* [3]. Each film was grown on Ag(100) substrate, and all processes were carried out under ultra-
high vacuum (base pressure $10^{-10}$ Torr) conditions. The choice to use Ag(100) as a substrate was made due to the minimal lattice mismatch of approximately 4% between Ag and CoO. As a result, the CoO film was epitaxial with orientation (100) and the intrinsic properties of the conversion reaction with this particular interface could be more effectively studied. Initially, the Ag(100) substrate was cleaned by Ar$^+$-ion sputtering at 1 kV. Surface order was refined by annealing the sample at 700 K. To verify surface order, Low Energy Electron Diffraction (LEED) was done on the sample.

After verifying the substrate surface was clean and ordered, CoO(100) was grown by means of a reactive electron-beam deposition of Co under an O$_2$ atmosphere of approximately $10^{-7}$ Torr while heating the Ag(100) substrate to 200°C. Upon deposition of an approximately 5 nm CoO film, LEED was performed once again to ensure epitaxial order of the film. The sample was then transferred in air to the XPS analysis chamber (Thermo Scientific ESCALAB 250Xi) for additional preparation.

To remove surface contamination after transfer, the sample was outgassed at 300°C and both the purity and stoichiometry were verified by XPS. Before lithiation, ARXPS scans of the Co2p, O1s, and Ag3d core-levels were taken in $10^9$ increments from surface normal to 50°. Core-level electrons were excited using x-rays from an Al-Kα source, which were monochromated to 1486.7 eV through use of Bragg diffraction. The spectrometer analyzed the energies of photoelectrons by use of a hemispherical analyzer, depicted in Figure 9.
The outer and inner hemispheres of the analyzer were kept at a potential difference with the outer hemisphere being more negative than the inner [6]. By varying the electrostatic bias between the two hemispheres, the range of energies of electrons to be measured could be selected for, as only a certain energy range of electrons would reach the multi-channel detector for analysis [13]. The selectivity of accepted electron energies, combined with consistency of x-ray energy allowed for precise measurements and calculations of core-level binding energies.

**Results and Discussion**

A survey XPS scan of the epitaxial CoO film on Ag(100), prior to lithiation is represented in Figure 10. Inset are core-level scans of the Ag3d and Co2p peaks.

*Figure 10: Survey scan of CoO(100) above Ag(100), with inset core-level scans of Ag3d and Co2p.*
To quantify the signal intensities of these core levels, background was subtracted and the area of each peak was normalized to account for its photoionization cross-section and the sensitivity of the electron detector. This procedure was done for each angle of measurement and the ratio of CoO intensity vs. Ag was then calculated. Figure 11 shows a theoretical fit of the experimental ratio of CoO:Ag based on the assumption that CoO is a continuous overlayer atop Ag(100).

![Figure 11: A comparison of experimentally-determined CoO:Ag ratio to the theoretical prediction for a 7 nm CoO layer on Ag.](image)

The model predicts that the CoO atop Ag was approximately 7 nm thick. A conspicuous observation was that the original model (seen in blue) greatly over-predicted the expected CoO:Ag ratio at large angles. A proposed source of this error was that elastic scattering of photoelectrons from the substrate off of atoms in the overlayer contributed to an increased Ag signal and thus an overall lower CoO:Ag ratio [4][9]. A schematic diagram of this process is represented in Figure 12. This explanation is plausible due to the fact that the CoO overlayer was thick, and Co is considered a high-Z atom. In Figure 11, the theory using corrections to EALs for this effect is represented by the black curve and provides a better fit to the data. An additional
explanation for deviation of the data from theory at large angle is the possibility of film roughness.

Conversion Reaction ARXPS

Upon exposure to atomic lithium, the CoO film was partially converted to Co\textsuperscript{0} and Li\textsubscript{2}O. The results of ARXPS on the sample after lithiation are summarized in Figure 13, which depicts the core levels of the sample as a function of angle.

Figure 12: A depiction of the elastic scattering effect from Ag off of CoO at glancing angles.

Figure 13: ARXPS summary of scans of (a) Co\textit{2p} (b) Li\textit{1s} (c) O\textit{1s} (d) Ag\textit{3d} core levels.
The signal from the Ag(100) substrate decreased in intensity as the detection angle became more grazing. This was anticipated by the ARXPS theory that as detection angle grows, the proportion of signal from surface layers grows as well. Another observation that can be made from the summary of ARXPS data is that for large angles, the intensity of the Co$^0$ peak grew while that of Co$^{2+}$ (characteristic of CoO) simultaneously decreased. There was an increase in the ratio of Li$_2$O$_2$ vs. Li$_2$O in the O1s peak and an increase in intensity of the Li1s peak for larger angles.

Quantitative information about the signal from Co$^{2+}$ and Co$^0$ was obtained by resolving the Co2p spectra into a linear combinations of Co$^0$ and Co$^{2+}$ reference spectra, as shown in Figure 14(a) for a single angle. Note that all of the Co2p spectra shown in Figure 13 could be fit with such a linear combination. Not only did this analysis allow for quantification of the relative amount of Co and CoO signal at each detection angle, but it also showed that no other phases of cobalt were present in the conversion reaction. Subtraction of background and integration of the
component peaks, as well as the peaks from the Ag3d, O1s, and Li1s core-levels provided quantification of the relative signal intensities detected at each angle.

In Figures 15(a) and (b) we plot the data retrieved by these analyses as a function of photoelectron detection angle. Figure 15(a) follows the angular variation of each signal’s intensity, while Figure 15(b) represents the angle dependence of the ratio of one signal to another.

The growth of Co$^0$ and Li$_2$O$_2$ signal with increasing detection angle can be seen in Figure 15(a). Also visible is the decrease in Co$^{2+}$ intensity and O1s corresponding to Li$_2$O and CoO with more glancing angles. Figure 15(b) shows an increasing proportion of Co$^0$ signal with respect to Co$^{2+}$ for glancing angle, suggesting that Co$^0$ is present atop CoO. Figure 15(b) also shows increased Li$_2$O$_2$ signal with respect to Li$_2$O for large angle, suggesting Li$_2$O$_2$ exists above Li$_2$O. The Li vs. Co$^0$ ratio remained relatively unchanged as a function of angle. The angular

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**Figure 15:** (a) ARXPS peak intensities of core-levels for lithiated CoO. (b) Various peak ratios as a function of angle.
dependence of these peak ratios imply that a complicated structure is present and that stratification of the reacted layers exists.

Because the Li vs. Co\(^0\) ratio remained relatively unchanged as detection angle grew, the possibility that Co and Li\(_2\)O existed in a heterogeneous overlayer was considered. Previous studies of the Li-CoO conversion reaction have also suggested phase segregation within the reacted layer [1]. Using the fractional coverage model summarized in Equation 12, ARXPS data of the Co:CoO ratio was fit in Figure 16.

![Figure 16: A comparison of experimentally-determined Co\(^0\):Co\(^{2+}\) ratio to the theoretical prediction for a 0.5 nm Co/Li\(_2\)O layer (31\% Co\(^0\)) on CoO.](image-url)

A theoretical fit of the experimental data on Co\(^0\) vs. CoO was achieved by assuming a predicted a 0.5 nm heterogeneous overlayer of Co\(^0\) and Li\(_2\)O with 31\% coverage by Co\(^0\). The 31\% fractional coverage of Co\(^0\) in the overlayer was motivated by the expected stoichiometry of one Co\(^0\) atom per Li\(_2\)O molecule. We calculate the expected volumetric fraction of Co\(^0\)

\[
\theta_A = \frac{M_{Co}/\rho_{Co}}{M_{Co}/\rho_{Co} + M_{Li_2O}/\rho_{Li_2O}} = 0.31
\]
where $\rho_x$ and $M_x$ are the mass density and molecular weight of each species.

Based on the ARXPS data, a tentative model of the phase front for the conversion reaction was devised in Figure 17.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure17}
\caption{A tentative model of the Li-CoO conversion reaction phase front.}
\end{figure}

ARXPS analysis suggests that upon lithiation, the surface region of the 7 nm CoO(100) film reacted to form a 0.5 nm heterogeneous overlayer of Co$^0$ and Li$_2$O with fractional coverages of 31% and 69%, respectively. ARXPS also provides evidence that above Co$^0$/Li$_2$O, a layer of Li$_2$O$_2$ was formed.
**Conclusions**

ARXPS study of the Li-CoO conversion reaction provided evidence of a uniformly-proceeding progression of the reaction front from surface down to substrate. The variation of peak intensity from the Co2p, O1s, Li1s, and Ag3d characteristic core-levels as a function of detection angle demonstrated complex layered structure of the converted sample. Analysis based on the Beer-Lambert Law allowed for modeling of thickness and morphology of these layers [4][6]. The results of ARXPS analyses are consistent with a mixed layer of Co$^0$ and Li$_2$O forming above CoO and under Li$_2$O$_2$; the results are consistent with suggestions of Co nanoparticles in a Li$_2$O matrix from previous studies [1]. Multiple questions arise after ARXPS analysis. At large glancing angles, the theoretical model appears to be insufficient due to overestimation of the observed ratio. This could be as a result of additional scattering effects, interface roughness, or other unknown variables. This provides motivation for additional investigation. There are also questions as to the implications of the surface overlayer of Li$_2$O$_2$ on the kinetics of the conversion reaction. Its effects on the diffusivity of Li in the reaction are unknown and should serve as a subject for further inquiry.

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