Competition between dissolution vs. ion exchange during low temperature synthesis of LiCoO₂ on carbon scaffolds

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Abstract

Deterministic design of electrodes is the concept of intentionally designing and controlling the electrode architecture to achieve high capacity and rate capability, leading to high power and high energy devices. Utilizing 3D conductive scaffolds for deterministic electrode design could unlock new applications for energy storage devices in structural energy storage and wearable electronics. One challenge is to obtain direct wiring of commercially-relevant electrode materials to 3D scaffolds such as porous carbon materials. For example, the synthesis of lithium metal oxide cathode materials requires high temperatures (>700°C) that exceed the stability of conductive carbon-based scaffolds (~400°C). In this work, we studied the aqueous chemistry of Co(OH)₂ to build a mechanistic understanding of a combined electrodeposition-hydrothermal synthesis along with mild heat treatment (<300°C) to obtain crystalline, layered LCO on 3D carbon scaffolds using only 3 feedstock materials. We established an understanding of how hydrothermal treatment pressure, temperature, duration, and LiOH concentration modulate the active synthesis mechanism and resulting LCO morphology. We find that in particular low hydrothermal pressure and high LiOH concentration prevent dissolution of precursor Co(OH)₂ to enable an ion-exchange of H⁺ from Co(OH)₂ with Li⁺ from solution to produce layered LCO while preserving the nanoflake architecture on the scaffold. We demonstrated the versatility of the ion-exchange process to coat a variety of electrode geometries and architectures. Overall, this research provides insight into the versatility, and limitations, of soft chemistry strategies to crystallize commercially relevant Liion cathode materials directly onto unique geometries for wide-ranging applications.



Table of Contents figure

Introduction

By 2030, energy storage for transportation applications is projected to account for most (4.3 TWh) of the 4.7 TWh total demand for Li-ion batteries.¹ This dramatic increase in energy storage demand for transportation provides an opportunity and need for rechargeable batteries that provide both maximum utilization of the active materials and multifunctionality. At the battery electrode level, controlling ion and electron transport pathways in electrode architectures via deterministic design could enable new electrode geometries for energy and power dense applications. Porous current collectors are interesting for deterministically designed electrodes due to their high surface areas for active material deposition and electrolyte infiltration compared to standard metal foils. Porous carbon scaffolds are particularly attractive because carbon is lightweight, abundant, and can be engineered to take on favorable mechanical properties for structural reinforcement and multifunctionality. A critical challenge in utilizing porous carbon scaffolds for Li-ion batteries is the deposition of commercially relevant lithiated transition metal oxide cathode material. As of 2024, over half of the market for Li-ion cathode materials comes from intercalation-based layered lithiated transition metal oxides such as LiCoO2 or LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂.² These oxide materials are synthesized using solid-state methods at temperatures > 700°C in air or oxygen-rich atmospheres.³ Porous carbon scaffolds are only stable only up to ~450°C in air, making the high-temperature processing of porous carbon scaffolds coated with lithiated metal oxides impossible in ambient environments.⁴ To circumvent this issue, Zhang et al. utilized a molten salt route to electroplate lithiated cathode materials onto geometric scaffolds including carbon foam at 260°C.⁵ However, the required oxygen-free atmosphere can be an impediment to scaling up manufacturing. Furthermore, the morphology of the cathode material deposit is different on each scaffold tested, making it difficult to control or predict the resulting electrode architecture across scales.

To utilize carbon scaffolds in deterministic electrode designs, we must develop novel manufacturing methods for integrating electrochemically active cathode materials into electrode architectures. Our previous work showed that electrodeposition of MoO₃ at ambient temperatures/pressures in aqueous solutions can be useful for fabricating electrode architectures with tunable mass loading and energy storage performance.⁶ Electrodeposition is a scalable method of obtaining metal oxides with direct adhesion onto a conductive substrate.⁷ For scalability, cost, and manufacturability, the ideal electrodeposition method for Li-ion battery materials would be performed from an aqueous electrolyte. This is challenging for intercalationbased cathode materials that require high synthetic temperatures, because synthesis of the active material must occur at temperatures within the stability range of the carbon scaffold while still producing the layered phase that is kinetically favorable for Li⁺ diffusion. In the case of LiCoO₂ (LCO) the layered polymorph ($R\bar{3}m$) typically requires high-temperature (>700°C) synthesis and is termed HT-LCO accordingly, while the spinel polymorph ($Fd\bar{3}m$) termed LT-LCO can be formed at temperatures as low as 20°C.^{8–13} The challenge lies in synthesizing phase-pure HT-LCO onto conductive carbon scaffolds at low temperatures. Hereafter, we use "LCO" interchangeably with layered or HT-LCO, and note LT-LCO as spinel LCO such where applicable.

Previous studies have combined electrodeposition and hydrothermal treatment methods to produce LCO conformally coating 3D carbon scaffolds.¹⁴ LCO can be obtained from cobalt hydroxide using hydrothermal methods at < 200°C. Amatucci and Larcher showed the synthesis of LCO powders via cationic exchange of CoOOH in an aqueous LiOH solution.^{15,16} The hypothesis was that the elevated pressure of the hydrothermal method lowers the synthesis temperature for LCO. Over the following decades, a wide variety of reaction conditions, solvents, oxidizing agents, and cobalt precursors were employed in hydrothermal reactions to produce LCO powders or films with varying morphologies and layered phase purities.^{11,17–22} Xia et al. utilized this understanding to develop a combined electrodeposition-hydrothermal method route for LCO

onto a carbon cloth scaffold at 380°C.¹⁴ They probed the influence of hydrothermal temperature on the resulting morphology, citing a competing mechanism of dissolution versus ion-insertion. Their findings suggested that an interconnected nanoflake morphology could be desirable for 3D electrode architectures. There remain open questions on the influence of other hydrothermal parameters beyond temperature on the resulting LCO morphology, and the applicability of this method to other conductive substrates.

In this work, we built upon the aqueous electrodeposition-hydrothermal method to synthesize LCO onto a range of commercially available conductive carbon scaffolds at less than 300° C.³ The possibility for low temperature synthesis of LCO suitable for carbon scaffolds is driven by the structural similarity of layered cobalt oxyhydroxide (CoOOH) and LCO phases (**Figure 1**). We hypothesized that under sufficiently oxidizing conditions, electrodeposited cobalt hydroxide Co(OH)₂ on a carbon scaffold could be exchanged with Li⁺ to yield LCO. Cobalt hydroxide has two polymorphs with different interlayer environments. Electrodeposition from aqueous solutions forms metastable α -Co(OH)₂ which may host intercalated water and/or anions (NO³⁻, Cl⁻), whereas β -Co(OH)₂ contains Co-OH edge-sharing octahedral units stacked compactly such that there are no guest molecules in the interlayer.²³ α -Co(OH)₂ transforms to β -Co(OH)₂ under highly alkaline conditions as interlayer molecules are expelled from the interlayer and the Co-OH slabs collapse.²⁴ β -Co(OH)₂ can be further oxidized to CoOOH, which is isostructural with layered LCO (both $R\overline{3}m$).



Figure 1. Crystal structures of precursors (α - and β -Co(OH)₂), solid intermediate (CoOOH), and product (LCO). Metastable α -Co(OH)₂ can convert to β -Co(OH)₂ under alkaline or oxidizing environments. CoOOH and LiCoO₂ are isostructural as R $\overline{3}$ m structures, with interlayer species of H⁺ and Li⁺, respectively.

Hydrothermal treatment can be used to provide oxidizing conditions necessary for ion exchange at low temperatures. A schematic of the full electrodeposition-hydrothermal process studied is shown in **Figure 2**. Our motivation was to understand the influence of the Co(OH)₂ precursor, the hydrothermal conditions, and the conductive carbon surfaces on the LCO properties and electrochemical behavior. We started by understanding the aqueous chemistry of α - and β - Co(OH)₂ powders and electrodeposits in concentrated Li salt solutions, and the propensity for ion-exchange between H⁺ in the bulk and Li⁺ in solution. We gradually added various driving forces to our analysis (electrochemical, thermodynamic) to determine the "softest" hydrothermal synthesis conditions necessary to create nanoflake LCO that could be widely applied for different porous carbon scaffolds. We observed a competition between a dissolution-recrystallization and ion-exchange reaction, and outlined the influence of each hydrothermal parameter on the reaction mechanism. We revealed that while temperature and synthesis duration can modulate particle size/thickness and in some cases prompt dissolution, the internal hydrothermal vessel pressure (controlled by the proportion of vessel volume occupied by LiOH, also called "vessel fill") and the concentration of LiOH are the most important variables in

determining the dominant reaction at play between ion-exchange and dissolution. We present reaction schemes for both mechanisms with intermediate reactions validated by control experiments. Finally, we demonstrate how to apply the ion-exchange synthesis method to create nanoflake LCO on a wide variety of carbon scaffolds. The result is an array of free-standing, 3D Li-ion cathode architectures made using only 3 feedstock materials (cobalt (II) nitrate, lithium hydroxide, carbon scaffold) and water at 200°C and without additional oxidizing, chelating, or dispersing agents.



Figure 2. Schematic representation of the electrodeposition-hydrothermal process studied in this work. Electrodeposition from an aqueous cobalt nitrate solution produces nanoflake α -Co(OH)₂ on carbon scaffolds. Hydrothermal treatment of these scaffolds in concentrated aqueous LiOH solution converts Co(OH)₂ to LCO. The vessel pressure and aqueous LiOH solution concentration control the competition between the dissolution and ion-exchange formation mechanism of LCO, resulting in nanoparticles and nanoflakes, respectively. The hydrothermal treatment equations show the hypothesized avenue for nanoflake formation through Co(OH)₂ oxidation and H⁺/Li⁺ exchange.

Experimental Methods

Co(OH)₂/LiOH titration

We made a series of solutions with varied molar ratios of Li⁺/Co²⁺ presented in **Table S1**. LiOH (Thermo Scientific Chemicals, anhydrous, 98% pure) was added to each vial in quantities described in **Table S1** along with 10 mL of deionized H₂O. LiOH was dissolved via magnetic stirring, and the pH of each solution was measured using a pH probe (Mettler-Toledo FiveEasy). After the initial pH measurement, 40 mg of Co(OH)₂ (Thermo Scientific Chemicals, 99.9%) were added to each vial and the vials were left to stir at 1000 rpm for 7 days at room temperature and an additional 7 days at 60°C. We took pH measurements after the time intervals listed **Table 1** below.

Time of pH measurement (days)	Description	
0	Before Co(OH) ₂ addition	
7	after stirring at room temperature	
14	after stirring at 60°C	

We used UV-Vis spectroscopy (Ocean Insight, OCEANHDX Miniature Spectrometer with a Quantum Northwest qpod 3 stage) to characterize the powders and supernatant in each via . To collect the samples for analysis, the vials were left on the benchtop for 3 days such that all solids settled at the bottom of the vial. The supernatant was extracted from the top of each vial and transferred to a quartz cuvette (Perkin Elmer, 10 mm). To repeat the measurement for the powders, the solutions were shaken and samples diluted by adding one drop of powder to deionized water. The spectra were collected from samples containing ~200 µL of powder solution from each vial added to 3 mL of deionized water in a quartz cuvette.

Carbon scaffold preparation & electrochemical surface area determination

The carbon scaffolds listed in **Table 2** were cut into 2 x 1 cm² rectangles and plasma cleaned before electrodeposition (Harrick Plasma PDC-32G). The plasma intensity and duration varied depending on the scaffold. Carbon nanotube foam electrodes were plasma cleaned for 3 minutes on low intensity, and all other scaffolds were cleaned for 5 minutes on high intensity.

The electrochemical surface area (ECSA) of each carbon scaffold was determined from cyclic voltammetry. The electrochemical cell was contained in a 25 mL three-neck glass round bottom flask. The working electrode was a ~1 cm² (geometric area) piece of the plasma-cleaned carbon scaffold, the counter electrode was a Pt coil (BioLogic), and the reference electrode was Ag/AgCl in saturated KCl (Pine). The electrolyte was 1 M Na₂SO₄ (Sigma-Aldrich, >99%) in deionized water. Cyclic voltammetry (CV) was performed between 0-0.6 V vs. Ag/AgCl for three cycles from 10 - 100 mV/s using a potentiostat (Biologic MPG). For each carbon scaffold, the double layer capacitance (C_{dl}) was calculated from the second cycle at 20 mV/s in a 200 mV stretch of the voltammogram where the current signal was purely capacitive (see **Figure S1** for an example). The ECSA was then calculated from assuming a surface-area normalized capacitance of 40 μ F/cm² for carbon:

$$ECSA(cm^2) = \frac{C_{dl}}{C_s}$$
(1)

where C_s is the specific double layer capacitance (assumed to be 40 μ F/cm²) and C_{dl} is the measured capacitance.²⁵ The ECSA was normalized by the mass of the carbon scaffold to yield the specific surface area.

Table 2. Carbon scaffolds and estimated electrochemical surface areas used to scale applied current during α -Co(OH)₂ electrodeposition.

Scaffold Type	Electrochemical Surface Area (m²/g)	Electrodeposition Current (mA)
CFOAM25 Carbon Foam	0.055	-2.00
Duocel RVC 10 PPI	0.069	-2.54
CFOAM35 HTC Graphite Foam	0.079	-2.89
Duocel RVC 30 PPI	0.099	-3.61
Duocel RVC 60 PPI	0.21	-7.74
Fuel Cell Earth AvCarb MGL190 Carbon Paper	0.55	-20.00
Duocel RVC 100 PPI	0.60	-21.94
Fiber Materials, Inc. Carbon Felt	1.4	-51.63
CNT Foam ^{6,26}	4.0	-144.99

Electrodeposition of α-Co(OH)₂ on carbon scaffolds

After the carbon scaffold was prepared according to the description above, a metal foil current collector was wrapped around one end of the scaffold. Either stainless steel foil or nickel tape was used, depending on the fragility of the scaffold. Stainless steel foil was sufficient for carbon paper, but nickel tape was required for more complex carbon scaffolds. The electrodeposition procedure was adapted from Yan et al.²⁷ The electrochemical cell consisted of a 25 mL three-neck glass round-bottom flask containing ~25 mL of 0.1 M Co(NO₃)₂ (Millipore Sigma, 98+%) in deionized water. A 1 cm² piece of each carbon scaffold served as the working electrode. Chronopotentiometry was used to deposit α -Co(OH)₂ on the carbon scaffold working electrodes. The electrodeposition procedure was optimized on carbon paper, and consisted of 3

minutes of -20 mA, 30 seconds of rest at open-circuit potential, and another 3 minutes of -20 mA applied current. This protocol produced mass loadings of ~2-4 g/cm² α -Co(OH)₂ on carbon paper. For electrodeposition on other carbon scaffolds, the same protocol was repeated but with the applied current density of -20 mA/cm² scaled to the experimentally obtained electrochemical surface area values shown in **Table 2**.

After electrodeposition, the electrode was rinsed thoroughly with deionized water and left to dry for at least two hours before hydrothermal treatment to convert the hydroxide to LCO. For the thick scaffolds with smaller pores (carbon felt, CNT foam) the electrodes were soaked in 100 mL of deionized water for an hour to completely remove the electrodeposition solution, and dried in a 60°C oven for at least two hours.

Preparing β -Co(OH)₂ on carbon paper

To prepare β -Co(OH)₂ on carbon paper, the electrodeposited α -Co(OH)₂ on carbon paper was soaked in 5 mL of 6 M KOH (Fisher Chemical) in deionized water for 12 hours at room temperature and pressure. After soaking, the electrode was soaked in 1000 mL of deionized water for several hours, checking the pH using a pH probe (Mettler-Toledo FiveEasy) every few hours and replacing the deionized water bath until the pH was neutral. After removing the electrode from the water bath, it was vigorously rinsed with deionized water and dried on a Kimwipe for 1 hour before transferring to a vacuum oven to dry for 12 hours at 60°C.

Synthesis of LCO

A hydrothermal reaction was used to convert the electrodeposited cobalt hydroxide on carbon scaffolds to LCO on carbon scaffolds. A 45 mL Teflon-lined acid digestion vessel (Parr Instrument Company) was used for all hydrothermal treatments. The hydroxide-coated carbon scaffolds were added to the Teflon vessel along with a solution of LiOH (Thermo Scientific, 98%) in deionized water. The electrodeposited portion of the scaffold was completely submerged in the

solution. The vessel was sealed and placed in a temperature-controlled oven (Baxter Constant Temperature Oven DN-63). We tested the influence of precursor phase (α or β), temperatures of 140°C and 200°C, durations of 15 hours and 120 hours, concentrations of 2M and 4.4M LiOH in H₂O, and solution volumes of 5 and 36 mL (denoted as 11% and 80% vessel fill, respectively) on the morphology and electrochemistry of LCO formed directly on carbon paper. The exact parameters employed in each iteration of the experiment are specified where the data is presented in the discussion below.

After the hydrothermal treatment, the vessel was removed from the oven and left to cool to room temperature for 2 hours in a closed fume hood. Once cooled, the electrodes were extracted from the vessel and soaked in 1000 mL of deionized water for 12 hours. The deionized water was replaced as many times as necessary until the solution was pH neutral. The electrodes were removed from the water bath and dried for 1 hour on a Kimwipe and subsequently at 60°C for 8 hours in air. Finally, all hydrothermally treated carbon paper electrodes were heated at 300°C for 8 hours in air in a box furnace (Thermo Scientific Lindberg Blue M).

Physical Characterization

X-ray diffraction (XRD) was used to characterize the electrodeposited cobalt hydroxide on carbon paper, using either a PANalytical Empyrean or X'Pert Pro X-ray Diffractometer in the standard Bragg-Brentano geometry with Cu-K α (λ = 0.54 Å) radiation. All XRD data shown in the main text was taken using the PANalytical Empyrean diffractometer, and the instrument used to collect data shown in the Supplementary Information is specified where presented in text. The electrode morphology was assessed using high-resolution scanning electron microscopy (Field Emission FEI Verios 460L or Hitachi SU8700.)

Electrochemical Characterization

Electrochemical characterization was performed in both flooded three-electrode cells and two-electrode coin cells. Any electrodes that were not heat treated at 300°C were dried in the vacuum oven for 12 hours at 60°C before transfer to a glovebox with < 1 ppm H₂O and O₂. The three-electrode electrochemical cells consisted of a 25 mL three-neck round bottom flask with the deposited carbon scaffold as the working electrode, and 3x1 cm² Li metal reference and counter electrodes. The electrolyte was 25 mL of 1 M LiClO₄ (Sigma Aldrich, 99.99%) in propylene carbonate (PC; Sigma Aldrich, anhydrous, 99.7%). Cyclic voltammetry (CV) at 0.1 mV/s for ten cycles was performed using a potentiostat (Biologic VMP). After cycling, the electrodes were rinsed thoroughly with dimethyl carbonate (DMC; Thermo Scientific, 99%) and left to dry on a Kimwipe overnight inside the glovebox. After the electrodes were completely dry, they were removed from the glovebox for further characterization.

The coin cells consisted of LCO deposited on carbon paper as the cathodes and Li metal as the anodes. After vacuum drying, 1 cm diameter electrodes were punched from the carbon paper with deposited LCO. These electrodes were assembled into 2032 coin cells in a glovebox with < 1 ppm H₂O and O₂. The coin cells also consisted of a Li metal chip (TMAX, battery grade) as the anode, a glass fiber separator (Whatman), a stainless steel 316 spring (MTI), two stainless steel 316 spacers (MTI, 0.5 mm) and 200 μ L of 1 M LiClO₄ in PC electrolyte. The cells were crimped with 0.8 Torr of pressure using a digital pressure controlled electric crimper (MTI, MSK-160E). Excess electrolyte was wiped away with a DMC-soaked Kimwipe and the cell was removed from the glovebox. Outside of the glovebox, the electrodes were wiped once again with an ethanol-soaked Kimwipe and cycled on a Biologic VMP potentiostat using cyclic voltammetry with a scan rate of 0.1 mV/s.

Discussion

Aqueous chemistry of Co(OH)₂ in alkaline solutions

The low temperature synthesis method involves hydrothermal treatment of Co(OH)2 in concentrated LiOH solution at elevated temperatures. We conducted a titration experiment to understand the interactions of β -Co(OH)₂ with different concentrations of aqueous LiOH solutions. We added a fixed mass of β -Co(OH)₂ powder to aqueous solutions of LiOH (**Figure 3a**). As the concentration of LiOH changed, so did the mol ratio of Li⁺/Co²⁺. The LiOH concentrations and corresponding mol Li⁺/Co²⁺ of each vial are shown in Table S1. The black curve in Figure 3a shows the pH of the aqueous LiOH solutions prior to adding β -Co(OH)₂. The pH increased rapidly for low LiOH concentrations, such that by 0.0215 M LiOH or 0.5 mol Li⁺/Co²⁺ the pH reached 12 and plateaued for higher LiOH concentrations. Upon addition of Co(OH)₂ to the LiOH solutions, there were no immediate changes (Figure S2, Day 1). After seven days at room temperature, there was a decrease in the pH of solutions at 0.043M LiOH (1 mol Li⁺/ Co²⁺) or less, with decreases most significant (to below pH ~10) under 0.00215M LiOH (0.05 mol Li+/ Co²⁺, Figure **3a** green inset, blue curve). After stirring the vials for 7 additional days at 60°C, there were three distinct pH regimes corresponding to different colors of powder solutions (Figure S2). We characterized the oxidation state of dissolved species and powders via UV-Vis spectroscopy, and the structure of the powders via XRD. Below 2 x 10⁻⁶ M LiOH, the pH of the solutions settled between 8.5-9.5 after all 14 days of stirring, and the powders turned black (Figures 3a and S2). In this pH regime, UV-Vis results in Figure 3b revealed no significant concentration of absorbing species present in the powders nor supernatant. XRD in Figure 3c confirmed the powder to be Co_3O_4 . The presence of Co_3O_4 and decrease in pH indicates deprotonation and partial oxidation of β-Co(OH)₂ in dilute LiOH (between 0-0.0046 mol Li⁺/Co²⁺). At higher LiOH concentration (between 0.00108-0.043 M and 0.025-1 mol Li⁺/Co²⁺) the β -Co(OH)₂ powders changed in color from pink to brown and the pH decreased to ~9.5-11.5 (Figure S2). The powders remained suspended in the supernatant immediately after stirring, settling completely after three days of rest without stirring. The XRD patterns of powder samples showed that β -Co(OH)₂ was the majority constituent. UV-Vis spectrum of the suspended powders (**Figure 3b**) showed absorption around ~420 nm, consistent with absorption of aqueous Co²⁺ species. Between 0.00108-0.00215M LiOH or 0.025-0.05 mol Li⁺/Co²⁺, there was no dissolved Co²⁺ in the supernatant (**Figure 3b**), indicating that β -Co(OH)₂ remained mostly in the solid state. At higher concentrations of 0.0215M-0.043M LiOH or 0.5-1 mol Li⁺/Co²⁺, the UV-vis spectra of the supernatant showed Co²⁺ species present in the solution. Pralong et al. reported that in alkaline solutions, Co(OH)₂ forms the dicobaltite anion, Co(OH)₄²⁻, which appears blue.²⁶ The authors reported a solubility limit of 0.048 mg/mL for β -Co(OH)₂ in 5 M KOH. Therefore, relatively small amounts of Co(OH)₄²⁻ are present from the spontaneous dissolution of β -Co(OH)₂. As the total OH⁻ concentration increases in the experiment, the magnitude of the pH decrease after stirring becomes smaller (**Figure 2a**, black compared to red). Specifically between 0.0215M-0.043M, we hypothesize that β -Co(OH)₂ partially dissolved in the aqueous LiOH solution to form CoOOH⁻.

For the sample at 0.215M LiOH or 5 mol Li⁺/Co²⁺, after 14 days of stirring a dark powder formed with negligible change in pH. The XRD pattern of this powder showed the $R\overline{3}m$ structure, similar to HT-LCO (**Figure 3c**). However, given the negligible change in pH during stirring, we hypothesize that both protons in Co(OH)₂ could not have been expelled into the solution. Instead, it seems likely that an ion-exchange process occurred with Li⁺ exchanging for one H⁺ along with the oxidation of Co²⁺ to Co³⁺. We hypothesize that one H⁺ in Co(OH)₂ fully exchanged with Li⁺ to form a mixed phase of LCO and CoOOH at 5 mol Li⁺/Co²⁺.

Since there is no significant pH change observed after 14 days of stirring for any concentrations above 0.0861M LiOH or 2 mol Li⁺/Co²⁺, we hypothesize that partial ion-exchange of one H⁺/Li⁺ began at 2 mol Li⁺/Co²⁺ and continued with higher extents of completion to 0.215M LiOH or 5 mol Li⁺/Co²⁺ (**Figure 3a**). The kinetics of the ion-exchange process are likely accelerated in higher concentrations of Li⁺.



Figure 3. Solid acid-base titration of powder β -Co(OH)₂ demonstrating regimes for formation of Co₃O₄ (green), partial dissolution of Co(OH)₂ (orange), and ion-exchange of H⁺/Li⁺ (red) under ambient, aqueous conditions. a) pH curve of samples in varied LiOH concentrations showing initial pH (black squares), pH after 7 days of stirring at room temperature (blue circles), and pH after 7 additional days of stirring at 60°C (red triangles). b) UV-vis spectra of supernatant and powder and c) XRD of powder from all vials.

Ion exchange of electrodeposited Co(OH)₂ on carbon paper

We first electrodeposited Co(OH)₂ onto carbon paper (CP), which served as a model lowsurface area conductive scaffold. During the cathodic electrodeposition from an aqueous solution of cobalt (II) nitrate, Yan et al. describes the reduction of nitrate anions and water near the scaffold to increase the local concentration of OH⁻ (**Figure S3**). Dissolved Co²⁺ reacts with OH⁻ and heterogeneously nucleates onto the carbon scaffold. The electrodeposition yielded a blue-green solid, characterized as α -Co(OH)₂ from XRD (**Figure 4a**) with a nanoflake microstructure (**Figures 2 and S4**). We designate this electrode as α -CoOH₂@CP. The most intense reflections in the XRD patterns come from the carbon paper scaffold (**Figure S5**), however reflections from the deposits do not overlap with those of the scaffold and are well resolved. The α -Co(OH)₂ nanoflakes grew radially outward from the surface to conformally coat the carbon fibers, and were well-adhered to the scaffold (**Figure S4**). To transform α -CoOH₂@CP into LCO@CP at ambient temperature, we attempted three methods: (1) ion exchange in 4.4 M LiOH, (2) conversion to β -Co(OH)₂@CP followed by ion exchange in 4.4 M LiOH, and (3) electrochemical ion exchange from a non-aqueous Li⁺ electrolyte. In the first ion exchange method, the resulting XRD pattern (**Figure 4b**) shows a mixed phase of CoOOH and LCO, indicating incomplete exchange. There are two interlayer (003) peaks ~19° suggesting two host species of different sizes. We also used cyclic voltammetry to identify the products. Different crystallographic phases of LCO show distinct electrochemical signatures in a non-aqueous Li⁺ electrolyte. Layered $R\underline{3}m$ HT-LCO or spinel $Fd\underline{3}m$ LT-LCO have similar XRD reflections but different cyclic voltammetry features: layered LCO has one redox couple between 3 - 4.2 V that is reversible ~3.9 V, and spinel has one reversible couple at ~3.7 V and one irreversible cathodic peak at ~3.2-3.4 V.^{29,30} After the ion-exchange (**Figure 4a,b**) the CV of the α -Co(OH)₂@CP electrode soaked in 4.4 M LiOH showed an oxidation peak at 3.8 V, attributed to Co oxidation and Li⁺ removal from an octahedral site (**Figure S6**). Upon applying reducing potentials, Li⁺ did not reinsert into the material.

In the second ambient temperature method, we first converted α -CoOH₂@CP to β -Co(OH)₂@CP prior to the Li⁺/H⁺ exchange. Strongly alkaline conditions drive the conversion of α -Co(OH)₂ to β -Co(OH)₂ as water and other molecules are expelled from the interlayer.²⁴ Soaking α -CoOH₂@CP in 6 M KOH leads to a color change from blue-green to brown, characteristic of β -Co(OH)₂. XRD confirmed this conversion (**Figure 4c**). β -Co(OH)₂@CP was then soaked in 4.4 M LiOH to drive the exchange of H⁺ with Li⁺. XRD (**Figure 4d**) showed that the product was a mixed phase of CoOOH and LCO, similar to α -Co(OH)₂@CP. However, the CV of this electrode in 1M LiClO₄ in PC was different, with an oxidation peak corresponding to Li⁺ removal from an octahedral site, and reduction peaks corresponding to Li⁺ insertion and restructuring in tetrahedral sites to form the *Fd*<u>3</u>*m* structure (**Figure S6**). These results show that by exposing different polymorphs

of Co(OH)₂ to high concentrations of LiOH under aqueous, ambient conditions, ion-exchange between H⁺ and Li⁺ to form CoOOH is possible, but is kinetically sluggish.



Figure 4. a) XRD of electrodeposited α-Co(OH)₂ shown predominantly α-Co(OH)₂ formed, with some β-Co(OH)₂ impurities. b) When α-Co(OH)₂ was soaked in 4.4M LiOH for 120h, H⁺/Li⁺ partial exchange occurred to form a mixed phase of CoOOH and LCO. c) Strong alkaline conditions of 6M KOH for 12 h force the conversion of α-Co(OH)₂ from a) to β-Co(OH)₂ on carbon paper. d) When β-Co(OH)₂ was soaked in 4.4M LiOH for 120h, H⁺/Li⁺ partial exchange occurred to form a mixed phase of CoOOH and LCO. CVs in Figure S6 depict differences in CoOOH structure ($R\bar{3}m$ vs $Fd\bar{3}m$) not discernible from XRD patterns. The XRD reference patterns used are: α-Co(OH)₂ (Liu et al.³¹) , β-Co(OH)₂ (CIF 1548810), CoOOH (CIF 90098844), HT-LCO $R\bar{3}m$ (JCPDS 000500653), LT-LCO $Fd\bar{3}m$ (JCPDS 010803830).

Since ion exchange in concentrated LiOH yielded partial exchange of H⁺ with Li⁺, we investigated whether electrochemical de-insertion of H⁺ followed by electrochemical insertion of Li⁺ would yield LCO by cycling α -Co(OH)₂@CP and β -Co(OH)₂@CP in a non-aqueous Li⁺ electrolyte (1 M LiClO₄ in PC). The electrode was first oxidized to remove H⁺, then reduced to drive Li⁺ insertion. The results in **Figure 5a** demonstrate negligible current response (<0.001 mA) for α -Co(OH)₂@CP over the course of 4 cycles, indicating no H⁺ de-insertion/Li⁺ insertion. However, cycling β -Co(OH)₂@CP similarly showed oxidation and reduction peaks corresponding to insertion/deinsertion of Li⁺ from the spinel Fd3m structure of LT-LCO (**Figure 5a**, orange). The magnitude of the oxidation and reduction peaks increased with cycling, suggesting increased utilization of the electrode. **Figure 5b** shows the ex-situ XRD pattern of β -Co(OH)₂@CP after cycling in the non-aqueous electrolyte, which depicts an almost complete transformation of the electrode to spinel LCO. From this and **Figure 4**, we observed that β -Co(OH)₂@CP was able to electrochemically insert Li⁺ and α -Co(OH)₂@CP could not, even when α -Co(OH)₂@CP soaked in LiOH had partial H+/Li⁺ exchange. These results suggest that the presence of interlayer molecules in α -Co(OH)₂ inhibited Li⁺ insertion, and prevented electrochemical H⁺ de-insertion.



Figure 5. Electrochemical insertion of Li⁺ into a) α -Co(OH)₂ and β -Co(OH)₂ on carbon paper in 1M LiClO₄ in PC electrolyte under ambient temperature and pressure. b) X-ray diffraction pattern of spinel LT-LCO on carbon paper formed after cycling β -Co(OH)₂ on carbon paper. Electrodes were cycled in a 3-electrode configuration.

Combining electrodeposition with hydrothermal synthesis to synthesize layered LCO

In the previous sections, we established the ability for partial oxidation and exchange of H^+ with Li⁺ in Co(OH)₂ at room temperature in concentrated LiOH, or using an electrochemical method. Previous work showed that LT- and HT-LCO can be synthesized by hydrothermally treating Co(OH)₂ with concentrated aqueous LiOH.^{14,18} However, there has not been a detailed investigation into the factors influencing the transformation of Co(OH)₂ into layered LCO under hydrothermal conditions. Here, we discuss the influence of four hydrothermal synthesis parameters employed in this study (pressure or vessel fill, LiOH concentration, temperature, and duration of hydrothermal treatment) on the resulting synthesis mechanism, morphology, and electrochemistry of LCO formed directly from α -Co(OH)₂ on carbon scaffolds. We utilized cyclic voltammetry to discern subtle differences in materials structure (LT- vs. HT-LCO), crystallinity, and morphology by analyzing features such as peak shape, position, coulombic efficiency (CE),

and peak separation (Δ V). In this work, all carbon paper electrodes were calcined at 300°C in air for 8h after the hydrothermal treatment.

Xia et al. reported a three-step electrodeposition, hydrothermal synthesis, and heat treatment of LCO on carbon cloth to convert α -Co(OH)₂ nanoflakes to LCO nanoflakes at low temperature (380°C).¹⁴ The interconnected nanoflake morphology was desirable to retain precursor mass on the carbon cloth scaffold in the absence of polymer binder. Here, we began by treating the electrodeposited α -Co(OH)₂@CP electrode with similar hydrothermal conditions (80% reactor fill, 2 M LiOH, 15 hours at 200°C). There is a distinct change in morphology after hydrothermal synthesis; the α -Co(OH)₂ nanoflakes transform into a dense agglomeration of nanoparticles on carbon paper as shown in Figures 6a-b. The stark change in morphology suggests a dissolution-recrystallization reaction took place during hydrothermal treatment. CV of this electrode in 1 M LiClO₄ in PC exhibited a sharp redox couple at \sim 3.9 V with a narrow peak separation of 40 mV (Figure 6c), characteristic of layered LCO. These peaks correspond to coupled Li⁺/e⁻ transfer from/to the material during the anodic/cathodic cycles. The sharpness and small hysteresis of the peaks indicate little dispersion in the site energies and good reversibility. which are indicative of a well-crystallized LCO material. The nanoscale microstructure allows for shorter electron transport and Li⁺ solid-state diffusion distances, which should facilitate fast kinetics. However, the current diminished rapidly upon cycling, as demonstrated by the low first cycle CE of 50%. We hypothesize that this decline in signal comes from detachment of the nanoparticles to the carbon paper matrix, leading to progressively decreased active material utilization with cycle number.



Figure 6. Influence of changing reactor fill (pressure) and LiOH concentration during hydrothermal treatment of electrodeposited α -Co(OH)₂ on carbon paper to produce LCO. SEM images and cyclic voltammograms of electrodes made using variable hydrothermal parameters of a-c) 80% fill of 2M LiOH, d-f) 11% fill of 2M LiOH, and g-i) 11% fill of 4.4M LiOH. The hydrothermal temperature and duration of treatment were kept constant at 200°C and 15 hours, respectively. All electrodes were cycled in 2032 coin cells.

The thermodynamic driving forces we applied during the synthesis of nanoparticle LCO were harsh enough to break down the precursor α -Co(OH)₂ nanoflake matrix. We decreased the pressure in the hydrothermal vessel by decreasing vessel fill from 80% to 11% and repeated the hydrothermal synthesis with all else held equal. Under these conditions, the synthesis yielded two

distinct morphologies (Figures 6d-e): irregularly shaped micron size particles surrounded by nanoscale (< 50 nm), roughly spherical particles. The cyclic voltammetry of an electrode made from these particles is shown in Figure 6f. The first cycle CE was higher (66%) than with the electrode made from particles from the high fill volume (50%) synthesis. This suggests that while the low fill volume synthesis yielded particles better adhered to the carbon paper, cycling stability was still a problem. The first cycle CV displays two sets of redox couples: at ~3.9V and at ~4.1V and ~4.2V that correspond to Li⁺ ordering to form a superstructure in LCO.³² Narrow peak separation implies fast electrochemical kinetics of the active material as described for Figure 6c, and we attribute this CV contribution to the nanoparticles in Figure 6d-e. Upon cycling, the 1/1' peak separation and width increased, and the peak current decreased, while the 2/2' peaks became less defined and eventually disappeared. This indicated a shift from an electrode with fast-ion insertion kinetics and structural homogeneity of the Li⁺ active sites in the solid toward an electrode with sluggish diffusion and poor utilization of the active material. Assuming D_{Li+} of 6.5 x 10⁻¹¹ cm²/s and linear diffusion with a potential-independent scan rate, the estimated Li⁺ diffusion distance in LCO is ~0.13 µm.33 Given that there were micron-sized particles in the electrode, evidence of sluggish solid-state diffusion in the CV is unsurprising.

Next, we maintained the lower fill volume while increasing the concentration of LiOH to 4.4 M. This synthesis yielded LCO with an interconnected nanoflake matrix (**Figure 6g-h**). In the corresponding CV (**Figure 6i**), this electrode had a higher first cycle CE (71%) than the electrodes from the other two syntheses, despite having larger peak breadth and separation for 1/1' (130 mV). The improved CE and cycling stability suggests that the adhesion of the LCO to the carbon paper was better. As a result, hydrothermal conditions yielding LCO nanoflakes resulted in the most favorable morphology for carbon paper-based electrodes.

The pressure and LiOH concentration in the hydrothermal vessel significantly influence the morphology and electrochemical behavior of LCO@CP electrodes. Given the two types of microstructures, we hypothesize that there are two different reaction mechanisms possible for the formation of LCO@CP from electrodeposited α -Co(OH)₂@CP. First we consider the nanoflake morphology of LCO@CP formed under low pressure and high LiOH concentration. Since this is similar to the microstructure of α -Co(OH)₂@CP, we hypothesize that these conditions favor an ion-exchange mechanism: proton and electron transfer reactions took place as H⁺ in solid Co(OH)₂ exchanged for Li⁺ from solution while Co²⁺ oxidized to Co³⁺ resulting in the formation of LCO. Under the absence of hydrothermal conditions, when electrodeposited α -Co(OH)₂ on carbon paper was left soaking in 4.4M LiOH on the benchtop we observed the exchange of one H⁺ for Li⁺ from solution validated by XRD in **Figure 4b**. During the titration experiment in **Figure 3**, we observed the same H⁺/Li⁺ exchange in the XRD pattern of commercial powders of β -Co(OH)₂ stirred in an aqueous solution of concentration 0.215M LiOH or 5 mol Li⁺/Co²⁺.

Hydrothermal reaction at high pressures and/or low LiOH concentrations leads to nanoparticle formation that is quite different from the nanoflake α -Co(OH)₂@CP precursor. Under these conditions, we hypothesize that the mechanism involves dissolution of α -Co(OH)₂ and redeposition of LCO. The titration experiment (**Figure 3**) confirmed the dissolution of Co(OH)₂ in dilute LiOH (0.0215-0.043 M LiOH, or 0.5-1 mol Li⁺/Co²⁺). Under hydrothermal conditions, we then propose that the soluble CoOOH⁻ reacts with Li⁺ to form LCO. The nanoflake morphology of LCO formed via the proposed ion exchange mechanism is favorable for coating porous conductive scaffolds such as carbon paper. Consequently, the next experiments investigated the influence of the hydrothermal treatment time (15 to 120 h) and temperature (140 C) while holding the pressure (11% reactor fill) and solution concentration (4.4 M LiOH) constant. **Figure 6g-i** shows the CV and microstructure of the LCO@CP electrode produced from a 15h of hydrothermal reaction whereas **Figure 7a** shows the corresponding results for an electrode produced from the 120h hydrothermal treatment. The shorter timescale yielded exclusively nanoflake morphology, while longer hydrothermal treatment led to a mixed microstructure containing both nanoflakes and

nanoparticles. This suggests that longer hydrothermal treatment leads to partial dissolution. Decreasing the hydrothermal temperature to 140°C for the same duration of 120h, led to the formation of nanoflakes that were thinner than those formed at 200°C (**Figure 7c vs Figure 7a**). This finding confirms that the hydrothermal temperature could be used to modulate LCO nanoflake thickness, as suggested by Xia et al.

Finally, we considered the influence of the Co(OH)₂ phase on the hydrothermal treatment by performing syntheses with either α -Co(OH)₂@CP or β -Co(OH)₂@CP as precursors. The SEM images of products from both syntheses (**Figure 7c, e**) show no significant difference in morphology between the resulting LCO. Since α -Co(OH)₂ converts to β -Co(OH)₂ in alkaline environments, it is likely that the conversion occurs "in situ" in the 4.4 M LiOH solution inside the hydrothermal vessel, which bypasses the need for an additional processing step.



Figure 7. Influence of hydrothermal temperature and Co(OH)₂ precursor phase on the synthesis of HT-LCO₂@CP. SEM images and cyclic voltammograms of hydrothermal syntheses performed using a-b) α -Co(OH)₂@CP at 200°C, c-d) α -Co(OH)₂@CP at 140°C, and e-f) β -Co(OH)₂@CP at 140°C. The vessel fill, LiOH concentration, and synthesis time were held constant at 11%, 4.4 M LiOH, and 120h, respectively. These electrodes were cycling in a 3 electrode configuration.

Toward deterministic electrode architectures for lithium-ion batteries

Thus far we established that free-standing, binder-free porous carbon paper electrodes featuring LCO with a nanoflake morphology exhibit superior electrochemical performance (CE and capacity retention) compared to the electrodes with a nanoparticle morphology. Within the synthetic space that produced nanoflakes, we observed patterns correlating hydrothermal treatment temperature and duration to preferential electrode performance. Holding the hydrothermal parameters that enable the ion-exchange mechanism and resulting nanoflake morphology as constants (11% vessel fill and 4.4M LiOH), Figure 8a depicts the cathodic capacity retention over 10 CV cycles as a function of hydrothermal treatment temperature and duration. Comparing the black curve to the blue curve in Figure 8a shows that the electrode produced under 120h at 200°C (Figure 7a) starts with a cathodic capacity close to theoretical for LCO (140 mAh/q denoted by the horizontal dashed line in **Figure 8**). This electrode retains more capacity at every cycle compared to the electrode that underwent 15h of treatment at 200°C. For a synthesis duration of 120h, the electrode produced at 200°C exhibits over 20 mA/g more cathodic capacity than the electrode at made at 140°C during the first cycle, but by the 10th cycle the performance gap narrowed such that the 200°C electrode was only marginally better. The narrow gap between the electrodes' cathodic capacity retention persisted through 20 CV cycles (Figure S7), but the electrode produced at 200°C for 120h exhibited slightly superior performance despite mild dissolution triggered by the longer synthesis duration. All electrodes show a slight improvement in CE during cycling, with the higher CEs for those synthesized at 120h (Figure 8b).

Despite the different hydrothermal treatment temperatures and durations, all samples experienced a capacity decline relative to the theoretical capacity within the first 10 cycles. Comparing pristine and ex-situ SEM after CV cycling revealed that for both 15h and 120h treatments, some LCO nanoflakes detached from the nanoflake matrix during CV cycling (**Figure S8 and S9**). These detached nanoflakes formed agglomerates and relocated to the surface of the existing nanoflake matrix, distancing themselves from the carbon paper and electronic percolation network in the electrode. Furthermore, we observed a difference in the continuity and adhesion of the LCO nanoflake matrix to the carbon paper when the hydrothermal treatment length increased from 15h to 120h. **Figure S8** shows that for the 15h case, the nanoflake matrix

remained fully covering the carbon paper scaffold in both pristine and cycled electrodes. The detached nanoflakes were decorated on the matrix's surface and did not protrude out from the electrode. Figure S9 shows that for the 120h case, the nanoflake matrix did not form a continuous coating on the carbon paper scaffold, with patches of carbon paper visible in the low magnification images (Figure S9 a and b). The higher magnification images in Figure S9c and d reveal that there were small gaps between the nanoflakes and carbon fiber where portions of the matrix were interconnected with itself but not contacting the scaffold. This detachment of the nanoflake matrix from the scaffold was even more pronounced after cycling, and compared to the electrode hydrothermally treated for 15h there were more nanoflake agglomerates decorating the surface of the matrix and stacking on top of one another to protrude far from the matrix's surface. The morphological rearrangement and nanoflake matrix detachment from the carbon paper both would result in disruptions to the electrode's electronic percolation network and achievable capacity during electrochemical cycling. Furthermore, for lower mass loadings (<1 mg/cm²) of electrodeposited a-Co(OH)₂, we observed densification of mass during the hydrothermal treatment which resulted in a patchy film that did not completely coat the carbon paper, as discussed further with Figure S10. These electrodes lacking an interconnected LCO film also experienced mass loss during cycling. Further work optimizing this method for low surface area and aspect ratio scaffolds such as carbon paper should focus on tailoring the amount of precursor α -Co(OH)₂ necessary to form a stable coating of LCO on the electrodeposited scaffolds. We also recommend exploration of methods to adhere the LCO to the carbon scaffold such as through pre-synthesis scaffold functionalization or treatment (i.e. roughening) or post-synthesis conductive polymer coatings.



Figure 8. a) Cycling stability and b) coulombic efficiency of LCO@CP electrodes made using variable hydrothermal treatment temperature and duration while pressure and LiOH concentration remained constant (11% vessel fill and 4.4M LiOH.) All electrodes were tested in a 3 electrode configuration. The dashed horizontal line indicates the theoretical specific capacity of LCO. The 120h treatment at 200°C produces an electrode with near-theoretical cathodic capacity during the first cycle, and superior capacity retention over electrodes produced at 140°C for 120h or 200°C for 15h.

Another potential avenue for performance improvement of the architectures could come from experimenting with the calcination procedure following hydrothermal treatment. In this work, all LCO@CP electrodes were calcined at 300°C in air for 8h after the hydrothermal treatment. This calcination step was not necessary to synthesize phase-pure layered LCO, as both pristine and calcined electrodes index well to the layered LCO structure and show sharp (003) and (104) peaks in XRD indicating high crystallinity (Figure S11). However, calcined electrodes exhibited slightly improved cathodic capacity retention and coulombic efficiency over pristine electrodes.

An important consideration for the viability of hydrothermal methods is the overall energy consumption relative to solid-state synthesis of cathode materials. While the electrodeposition-

hydrothermal method is a batch process in which many electrodes can be made simultaneously, further work is necessary to assess if the decrease in LCO synthesis temperature equates to energy savings in the overall manufacturing process on a per-mass basis. Some energy calculations of Li and Na ion materials synthesis have shown that although solvothermal processes occur at substantially lower temperatures, the energy required can be comparable or larger than what would be required to synthesize materials from the solid-state.^{34–36} In the method outlined here, energy-intensive steps include water splitting to produce OH⁻ driving the chemical precipitation of Co(OH)₂ during electrodeposition and heating LiOH solution during hydrothermal treatment. Regardless, in this work we emphasize that the primary utility of the electrodeposition-hydrothermal method is to conformally coat carbon scaffolds that are not stable at solid-state synthesis temperatures.

Versatility of the method with other porous carbon scaffolds

We finally demonstrate the versatility of the combined electrodeposition-hydrothermal method to produce LCO at 200°C on eight other commercially available carbon scaffolds. These scaffolds varied in geometry from foam-like to fiber-like microstructures. The processing protocol consisted of electrodepositing α -Co(OH)₂ onto each carbon scaffold and hydrothermal synthesis in 4.4 M LiOH for 15 hours at 200°C with 11% reactor fill. There was no final annealing step at 300°C. The electrodeposition current was adjusted for each scaffold based on its experimentally-determined electrochemical surface area (ECSA) (Table 2). After electrodeposition, all scaffolds were completely coated by α -Co(OH)₂ nanoflakes (Figures S12-20). SEM images for four representative carbon scaffolds coated with LCO are shown in Figure 9. SI Figures S12-20 and S21 provide the complete microstructural and cyclic voltammetry characterization for the scaffolds, respectively. Cyclic voltammetry confirmed the presence of LCO on seven scaffolds, although with varying degrees of electrochemical reversibility (Figure S21). We could not reliably connect electrodes made from the most porous Duocell RVC 10 and 30 ppi scaffolds to an

30

electrochemical cell as they became too brittle following the hydrothermal treatment. They both appear to be coated with LCO in SEM images (**Figures S13 and S15**). The low magnification images in the top row of **Figure 9** show the bare carbon scaffolds. The ECSA and aspect ratio of the scaffold influenced the morphology of the LCO, which became more obviously nanoflake-like with increasing ECSA and aspect ratio.



Figure 9. SEM images of LCO deposited on four different commercially available porous carbon scaffolds: a) CFOAM25 foam, b) Duocel RVC 60 PPI, c) carbon felt, and g) CNT foam. The top row of low magnification images are of the bare scaffolds. All synthesis involved electrodeposition of α -Co(OH)₂, hydrothermal treatment in 4.4 M LiOH for 15 hours at 200°C with 11% reactor fill.

The LCO nanoparticles shown on the lower ECSA and aspect ratio scaffolds (CFOAM25 and Duocel RVC 60 ppi, respectively) resembled products of a dissolution-recrystallization reaction. However, after the hydrothermal treatment, the LiOH solution was free of particles, contrary to the dark, cloudy solution in syntheses that followed the dissolution/deposition mechanism for LCO formation. Therefore we hypothesize that ion-exchanged LCO was formed on the low ECSA scaffolds, however the lower mass loadings resulted in smaller particles not easily identified as nanoflakes by inspection as described in the discussion of **Figure 8** and **Figure S10**.

Conclusions

In this work, we developed and characterized a combined electrodeposition-hydrothermal method to deposit HT-LCO from α -Co(OH)₂ on different porous carbon architectures at low temperatures (200°C) to preserve the carbon scaffold. We first investigated the aqueous chemistry of α - and β - Co(OH)₂ in concentrated LiOH aqueous solutions under ambient conditions. We demonstrated that H⁺/Li⁺ ion-exchange is possible in both bulk powder and electrodeposited α - and β - Co(OH)₂ under high concentrations of LiOH (>0.215M LiOH or mol Li⁺/Co²⁺). The results also showed a pH and Li⁺ concentration regime for partial dissolution of β - Co(OH)₂ to CoOOH⁻. We also attempted H⁺/Li⁺ ion-exchange in a non-aqueous Li⁺ electrolyte and found that H⁺/Li⁺ exchange could take place electrochemically but yielded spinel LCO.

We next presented the influence of hydrothermal treatment parameters such as vessel pressure, LiOH concentration, treatment duration, temperature, and Co(OH)₂ polymorph on the synthesis of freestanding LCO@CP electrodes as a model architecture. By independently varying synthesis parameters, we were able to illustrate the individual effects of each parameter on the resulting morphology and electrochemical behavior. This illuminated the possible synthesis mechanisms. The hydrothermal vessel pressure (controlled by vessel fill) and LiOH concentration are both key determinants of the synthesis mechanism: higher pressures (80% vessel fill) and low LiOH concentrations (< 2 M LiOH) favor dissolution of the α -Co(OH)₂ precursor, followed by recrystallization to form LCO nanoparticles on the scaffold surface. While the HT-LCO was well-crystallized as evidenced by cyclic voltammetry and XRD, electrodes with this morphology did not exhibit good cycling. We hypothesize that in this case, the nanoparticles did adhere well to each

other or the scaffold, leading to severe capacity fade. Under lower pressures (11% vessel fill) and higher LiOH concentrations (4.4 M LiOH), LCO forms via an ion exchange and oxidation mechanism directly on the scaffold. This process preserves the nanoflake morphology of the α -Co(OH)₂ precursor, which was interconnected and well-adhered to the scaffold. Changing the duration and temperature of the hydrothermal treatment also modulates the reaction mechanism (i.e. longer duration promotes partial dissolution) and fine-tunes the morphology (i.e lower temperature causes thinner nanoflakes). We used this method to deposit nanoflake LCO on nine different commercial carbon scaffolds with varied surface areas, aspect ratios and porosities without compromising the integrity of the scaffolds, demonstrating that the processing conditions are suitable for a wide range of architectures. Future work to improve this method should focus on 1) strategies to enhance the adhesion of the nanoflake LCO to carbon scaffolds, and 2) understanding how to engineer the electrodeposition of α -Co(OH)₂ to accommodate for the densification of material during the ion-exchange to produce an ideal coating of LCO with favorable ion and electron transport properties.

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