High-Purity Lithium Metal Films from Aqueous Mineral Solutions

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ABSTRACT: Lithium metal is a leading candidate for next-generation electrochemical energy storage and therefore a key material for the future sustainable energy economy. Lithium has a high specific energy, low toxicity, and relatively favorable abundance. The majority of lithium production originates from salt lakes and is based on long (>12 months) periods of evaporation to concentrate the lithium salt, followed by molten electrolysis. Purity requires separation from base metals (Na, K, Ca, Mg, etc.) which is a time-consuming, energy-intensive process, with little control over the microstructure. Here, we show how a membrane-mediated electrolytic cell can be used to produce lithium thin films (5–30 μm) on copper substrates at room temperature. Purity with respect to base metals content is extremely high. The cell design allows an aqueous solution to be a continuous feedstock, advocating a quick, low-energy-consumption, one-step-to-product process. The film morphology is controlled by varying the current densities in a narrow window (1–10 mA/cm²), to produce uniform nanorods, spheres, and cubes, with significant influence over the physical and electrochemical properties.

§ INTRODUCTION

Safe rechargeable batteries with higher specific energy are crucial for a wide variety of applications,1–7 and lithium metal is one of the most attractive anodes because it is the lightest and most electropositive metal, possessing a theoretical specific coulometric capacity (3860 mAh/g) 10 times greater than that of the graphite anodes used in lithium-ion batteries (372 mAh/g), a density of 0.59 g/cm³, and a high negative reduction potential of −3.040 V versus the standard hydrogen electrode.6,8–12 The emergence of lithium battery technologies, for which a range of electrolytes and cathodes is contemplated, has been hailed as the likeliest group of successors to the current multibillion dollar lithium-ion battery paradigm.13 Such technologies include lithium–sulfur14–16 and lithium–air/oxygen configurations.17–19 A major problem that emerges when lithium metal anodes are cycled is the growth of dendrites.1,6,12,20–24 The passage of current through these structures can short the battery or cause catastrophic failure.23 Efforts to prevent dendrite growth have primarily focused on blocking these protrusions.8,16,20,22,25–27 Li dendrite growth has been shown to stem from impurities in the Li metal electrode, which facilitate the nucleation of subsurface dendritic structures, and removal of such impurities can inhibit dendrite growth, although the exact impurity that catalyzes dendrite growth remains unclear.10 What is clear, however, is that producing lithium with greater control over purity and morphology will be critical for the success of energy storage technologies built from a lithium anode platform.

About 75% of current lithium production originates from brines in the salars-evaporite basins (dried salt lakes) in the high Andes of Chile, Argentina, and Bolivia.28 This lithium is highly diluted, requiring extensive extraction operations and a copious water supply. It is then concentrated through solar evaporation (18–24 months). The base metal contaminants depend on the original brine content, typically Na, K, Ca, and Mg, with Na being a major impurity of around 1%.29 Lithium metal with purities in the range of 99.5–99.99% can be subsequently manufactured using electrowinning from molten eutectic LiCl–KCl salt electrolysis at around 500 °C.30 The energy requirements (35–40 kWh kg-Li), combined with the production of anhydrous lithium chloride feedstock, make for an energy-intensive process.31 Producing high-purity lithium metal at the level suitable for energy storage technology (>99.99%) is therefore challenging. For development into form factors suitable as electrodes, the lithium is extruded from an ingot into a foil typically limited to thicknesses above 100 μm and often prepared as a lithium–aluminum alloy foil, to maintain mechanical strength. There are inherent difficulties associated with preparing extruded thin lithium metal films <100 μm, with little possibility for control over microstructure. An alternative, that of a pure thin film-on-substrate, would be highly desirable for next-generation battery researchers and lithium metal battery manufacturers alike.

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Supporting Information

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Here, we demonstrate the ability of producing high-purity (with respect to metals content) lithium thin films in a variety of highly uniform and tunable morphologies at room temperature by an electrolytic cell. Dendrite-free thin films of high purity with respect to base metal contaminants are electrolytically deposited on a copper anode. The method is a low energy consumption approach when compared to the existing lithium manufacturing process. The cell design relies on a lithium-ion conducting solid-state membrane to transport Li\(^+\) ions from an aqueous mineral solution (lithium carbonate or other suitable lithium containing feedstock) to an organic conducting electrolyte in the absence of additives.\(^{32-36}\) The morphology of the lithium can be precisely tuned as a function of current density in an extremely narrow window (1 – 10 mA/cm\(^2\)). The morphologies produced are spheres, cubes, and, most significantly, rods—an array of uniform, self-aligned, tightly packed, perpendicularly oriented rods with diameters of 300 nm. Purity and structural characterization of the three Li metal film morphologies (self-aligned nanorods, spheres, and nanocubes) were characterized via scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectrometry (ICP-MS). To evaluate the electrochemical performance of the different Li metal film morphologies for Li-ion batteries, two-electrode cells, in the form of standard CR-2032 coin-type cells, were fabricated and compared to Li metal foil as a standard. The rods, with lengths in excess of microns (10 – 200 \(\mu\)m), give rise to smooth films of lithium with an iridescent blue color. Microscopy of the rodlike array is reminiscent of the arrangement of chitin in morpho butterfly wings, the cause of structural coloration and their blue color. We present and advocate an additive-free method to produce high-purity lithium suitable for electrochemical applications, including energy storage, in which pure, dendrite-free electrodes with morphological control over a small range of current densities can be accomplished in one step (Figure 1).

■ RESULTS AND DISCUSSION

To evaluate the purity of the electrodeposited lithium metal, samples were analyzed independently by Intertek (Intertek...
Group PLC) for ICP-MS. The lithium purity was determined to be 99.985 wt % against a scan of 69 isotopes, 99.996 wt % on a metal basis. A complete list of the elements scanned and their concentration is presented in Table S1, Supporting Information. The major impurities in the film were silicon (69 ppmw), sulfur (19 ppmw), sodium (13 ppmw), and phosphorus (10 ppmw). The source of silicon impurities is systemic: it is known for ICP-MS and confirmed by Intertek that the silicon-rich environment of the ICP torch regularly causes significant background problems in the analysis. Consequently, the reported silicon concentration is unreliable because of these high background levels. The small amount of sulfur likely stems from the Cu foil pretreatment step, where trace amounts of sulfuric acid might have adsorbed onto the Cu surface. Phosphorus contaminants are from the LiPF₆ salt in the organic electrolyte solution that was not completely removed from dimethyl carbonate (DMC) rinse after deposition.

By controlling the lithium deposition rates, distinct morphologies of deposited Li can be prepared, as shown in Figure 2A–C. The deposition rates of −3, −5, and −7 mA/cm² formed Li rods, spheres, and cubes respectively. The low-magnification images (Figure 2) show uniform structures, which is consistent across the entire 3 cm × 3 cm electrode surface. The electrochemically deposited films deposited at −3 mA/cm² form self-aligned, highly compacted nanorods with hemispherical tips with diameter of about 300 nm. See also Figure S1, Supporting Information. The Li spheres, deposited at −5 mA/cm², exhibited a higher surface roughness and an

Figure 2. SEM images of electrolytically deposited Li films on 9 cm² copper foil under different conditions: (A) rods, (B) spheres, (C) cubelike morphology. In the case of the rods, a fractured zone was imaged to illustrate the extent of depth and aspect ratio.

Figure 3. Pristine nanorod film under an argon atmosphere and X-ray diffractograms of the lithium film before (red) and after 15 and 30 min (blue and green, respectively) exposure to air.
average particle size of $\sim 1 \mu m$. The Li cubes, deposited at $-7 \text{ mA/cm}^2$, had an average size of $\sim 100 \text{ nm}$. This is a somewhat unique observation of electrodeposited Li metal with sphere and cube morphologies, and of self-aligned rod morphologies without any additives.\textsuperscript{5,6}

The deposition of relatively thick layers of highly crystalline Li metal is further confirmed in the XRD pattern, by a sharp peak at 35.9° $2\theta$ (PDF #15-0401), as shown in Figure 3. It also shows the formation of low-crystalline LiF, expected to be a part of the solid—electrolyte interphase (SEI) layer, defined by broad peaks of low intensities at 38.7 and 45.0° $2\theta$ (PDF #04-0857). No sign of lithium oxidation is found in the initial material. LiF is thought to play a critical role in the formation of nanorods.\textsuperscript{8,37} Following exposure to air during the XRD measurement, the sample begins to oxidize, visible in the diffractograms taken after 15 and 30 min of exposure (Figure 3). An expected reaction with air moisture results in the formation of LiOH (peaks at 32.4, 35.6, and 51.4° $2\theta$ PDF #32-0564) as a hydrolyzation product, following the reaction $2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2$. The intensity of LiOH peaks increases with longer exposure times. The hydrolysis is ultimately observed visually by the reactive lithium film turning white.

X-ray photoelectron spectroscopy (XPS) is a proven powerful technique in the characterization and compositional analysis of electrode materials, including electrochemically deposited lithium.\textsuperscript{38,39} To acquire complementary information about the nonmetal contents, understand the composition of the solid—electrolyte interphase (SEI) layer, and estimate the SEI layer thickness, high-resolution XPS spectra were recorded for Li rod films (Figure 4A,B). Samples of freshly deposited lithium films were rapidly transferred from inert atmospheres to the XPS chamber to minimize the effect of air exposure. XPS was then recorded on pristine samples, followed by Ar$^+$ sputtering to obtain depth profile information regarding the film from the surface (0 nm), down to 700 nm with successive intervals. Nonsputtered, pristine samples reveal the presence of Li as the main element, together with four impurities—F, O, C, and P (Figure 5a,c). Two of them—C and P, which originate from the organic solvent and electrolyte (or their decomposition products)—completely disappear after the Ar$^+$ sputtering of the topmost 10 nm of the film, suggesting localization of these elements to the film surface (Figure S2, Supporting Information). XPS analysis is able to reveal detailed information regarding the nature and composition of the film: peak deconvolution of the first scan in the Li 1s region shows that the lithium metal (Li$^0$) signal appears prior to Ar$^+$ sputtering, suggesting an SEI layer thickness of $<10$ nm (Figure 4A). The top surface layer consists of lithiated products of decomposed DMC (viz. CH$_3$OLi, CH$_3$COOLi), organic electrolyte salts (viz. LiPF$_6$, LiPO$_x$F$_y$), LiF, and LiOH. The presence of LiOH is...
most likely due to the reaction of Li metal with water vapors when it is exposed to air during the transfer to XPS machine. No evidence of pure DMC on the lithium surface was found in the C 1s region (see Figure S1, Supporting Information), indicating (i) complete DMC removal upon vacuum drying at ~30 psi in the glovebox anechamber, and/or (ii) post reaction of DMC with Li at the surface. After sputtering, LiF and LiOH are the main impurities observed in the sample. The XPS spectra in the O 1s region also reveal the presence of Li2O (Figure 5a), which may be due to the exposure of LiOH to high-energy Ar+ sputtering beams, following the reaction 2LiOH → heating → Li2O + H2O, and therefore the presence of Li2O may be due to the analysis procedure. It is therefore deduced that fluorine is the major impurity for the electrolytically deposited lithium film in a H2O/O2-free environment. Considering the observation of two separate crystalline structures of Li and LiF, as evidenced by XRD and XPS, and consistent amounts of LiF through the sample, we suggest that lithium rods are formed by a pure lithium metal enveloped by a thin layer (<10 nm) of LiF. This layer is expected to act as a barrier, preventing Li rods from growing in and keeping them aligned in parallel.14 When used as an electrode for energy storage applications, the LiF may also play a beneficial role in the context of Li-ion conductivity, acting as a protective layer against formation of the SEI layer due to electrode exposure to organic electrolyte and preventing dendrite growth upon cycling. Similar qualitative results were obtained for the film of Li spheres, but with a thicker SEI layer—up to 40 nm (assuming a sputtering rate of 4 nm/min; see Figure S3, Supporting Information). A LiF signal appeared only after the first sputtering. Moreover, C and P elements were found even after 21 min of sputtering (~84 nm in depth). It should be noted that these results might be affected by surface roughness of the film, which causes nonuniform exposure to the ion beam and, consequently, uneven etching of the film.

To demonstrate the applicability of the lithium films and their morphologies, preliminary electrochemical testing was conducted. It was anticipated and observed that precise control over lithium morphology during deposition and growth can affect coulometric capacity. As a preliminary investigation of performance, the electrolytically deposited lithium films were tested using an asymmetric Li symmetric cell (for instance, 1 M electrolyte solution of LiPF6 in ethylene carbonate (EC)/DMC/diethyl carbonate (DEC) in 4:2:4 by volume ratio is optimized to be used in lithium manganese oxide batteries).

### CONCLUSIONS

In conclusion, we have prepared lithium thin films at room temperature by an electrolytic cell. The morphology of the lithium can be precisely tuned as a function of current density in an extremely narrow window (1–10 mA/cm²). Dendrite-free thin films of high purity with respect to base metal contaminants are electrolytically deposited on a copper anode. The cell design relies on a lithium-ion conducting solid-state membrane to transport Li+ ions from an aqueous mineral solution (lithium carbonate or other suitable lithium containing feedstock) to an organic conducting electrolyte in the absence of additives. The most significant morphology is an array of uniform, self-aligned, perpendicularly oriented rods with diameters of ~300 nm that give rise to smooth films of lithium with an iridescent blue color.

### EXPERIMENTAL SECTION

**Characterization.** X-ray powder diffraction (XRD) patterns were recorded with a D8 Discover X-ray diffractometer (Bueker Corporation, Cillerica, MA) using Cu Kα radiation (λ = 1.54 Å) with 0.01° 2θ steps. SEM analysis was performed on a Zeiss Supra 50 VP (Carl Zeiss SMT AG, Oberkochen, Germany) using an accelerating voltage of 3 kV. Quantitative elemental analysis was performed by Intertek using a Thermo Scientific Element 2 SF-ICP-MS. Sample solutions were transported to the ICP torch using a PFA cyclonic spray chamber configured with a PFA Meinhard nebulizer and a 2.0 mm alumina injector. A scan of 69 isotopes was performed. The instrument calibration standards for ICP-optical emission spectrometry analysis were matrix matched to the samples prepared for analysis. The quantitative trace analysis routine consisted of eight standards prepared in the range of 0.1–20 parts per billion to bracket the suspected levels in the sample. The calibration standards were prepared using Inorganic Ventures milligram per liter (10 mg/L) multielement and single-element stock standards. The samples of lithium deposited on copper sheets were transferred to 100 mL beakers containing aliquots of chilled deionized water. After the lithium dissolved, the aliquots were combined into a 50 mL graduated tube. The sample was diluted to 50 mL with deionized water. Concentrated nitric acid (0.5 mL) was added to the sample. XPS analysis of lithium rods on copper substrates was performed using a PHI VersaProbe II spectrometer (Physical Electronics Inc.) employing a 200 μm monochromatic Al Kα X-ray beam with an operating pressure of ~2 × 10⁻⁹ Torr. The emitted photoelectrons were collected using a 180° hemispherical electron energy analyzer. Samples were analyzed at a 45° takeoff angle between the sample surface and the path to the analyzer. High-resolution spectra were taken at a pass energy of 50 eV and with a step size of 0.8 eV for survey and 0.05 eV for high-resolution regions. A beam of 5 kV argon ions...
Electrochemical Testing. To evaluate the electrochemical performance of the produced lithium films as anode materials for secondary battery applications, two-electrode cells, in the form of standard CR-2032 coin-type cells (MTI Corporation, Richmond, CA), were assembled in an Ar-filled glovebox. The produced lithium metal films of different morphologies (spheres, rods, and cubes) were compared to commercial lithium foil (99.9%, Alfa Aesar, Ward Hill, MA). Composite graphite, single coated on copper foil (loading of 60 g/m²; MTI, Richmond, CA), was used as the working electrode. A 25 μm trilayer polypropylene–polyethylene–polypropylene membrane (Celgard LLC, Charlotte, NC) was used as the separator material. Then, 1 M LiPF₆ solution in a mixture of ethylene carbonate (EC), DMC, and diethyl carbonate (DEC) in 4:2:4 by volume ratio (MTI, Richmond, CA) was used as the battery electrolyte solution. The coin cells were tested in the galvanostatic mode within the voltage range of 0.01–1.5 V versus Li, using an eight-channel battery cycler (BST8-MA, MTI, Richmond, CA) to estimate current density, graphite anode compartment of the cell, was prepared by dissolving lithium carbonate (Li₂CO₃) in sulfuric acid solution. Electro-lytic deposition was conducted at room temperature using a galvanostatic mode within the voltage range of 0.01–1.5 V versus Li, using an eight-channel battery cycler (BST8-MA, MTI, Richmond, CA) as a cathode and, simultaneously, the electrolytic deposition of lithium metal was carried out using an electrochemical cell, the schematic of which is depicted in Figure 1.40 The cell comprises a stainless steel counter electrode (anode), a copper foil working electrode (cathode), and a lithium-ion conducting glass ceramic membrane of the form Li₁+δAl₃Ti₂Ge₂Si₆P₈O₂₃ (LGC-IC, Ohara Corporation), which separates the two electrodes and electrolyte solutions. A 125 μm-thick copper foil (Goodfellow Cambridge Ltd, England) was used as a cathode and, simultaneously, the substrate for lithium metal deposition. Lithium hexafluorophosphate (LiPF₆) solution in dimethyl carbonate (DMC, Sigma-Aldrich, St. Louis, MO) was used as the organic electrolyte. An aqueous electrolyte, circulating through the anode compartment of the cell, was prepared by dissolving lithium carbonate (Li₂CO₃) in sulfuric acid solution. Electrolytic deposition was conducted at room temperature using a potentialstat/galvanostat power supply (Reference 3000, Gamry Instruments, Warminster, PA), with aqueous electrolyte continuously circulating through the cell. Lithium metal films were prepared under galvanostatic conditions, a current between −1 and −10 mA/cm² was chosen, depending on the desired lithium film morphology.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01501.

Figure S1: SEM images of nanorods at a range of magnifications and orientations; Figure S2: high-resolution XPS spectra of lithium rods on a copper substrate, showing C 1s and P 2p regions, and depth profile; Figure S3: high-resolution XPS spectra of the sphere morphology on copper showing Li 1s, O 1s, F 1s, C 1s, and P 2p regions and depth profile; Table S1: ICP-MS results of lithium films performed by Intertek using a Thermo Scientific Element 2 SF-ICP-MS (PDF)
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