Solvent-Processed Metallic Lithium Microparticles for Lithium Metal Batteries

Sipei Li,†∥ Han Wang,†∥ Wei Wu,‡ Francesca Lorandi,†∥ Jay F. Whitacre,*∥§ and Krzysztof Matyjaszewski*†

†Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States
‡Department of Materials Science & Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States
§Scott Institute for Energy Innovation, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

Supporting Information

ABSTRACT: Foils that serve as Li metal anodes suffer from poor cycling and safety concerns due to dramatic volume changes and dendrites formation. In this work, we report a convenient solvent-processed approach to prepare and extract high-purity lithium metal microparticles (Li MPs). As a proof-of-concept, a freestanding porous Li MPs/carbon nanotubes composite anode (LMCA) based on mechanically bound interconnected Li MPs was prepared and showed an improved cycling performance compared to a Li foil anode, as the created 3D porous structures can alleviate electrode volume changes and increase electroactive surface areas.

KEYWORDS: Li metal microparticles, solvent process, cycling performance, composite anode, lithium metal batteries

Lithium metal anode batteries (LMBs) are widely regarded as the most promising next-generation high-energy-density lithium-based solution. Lithium metal has the highest negative electrode potential (−3.05 V vs H2/2H+) and specific capacity (3860 mAh/g) and can be paired with high-energy non-lithiated cathodes, such as sulfur and oxygen. Conventional Li metal anodes are in the form of a plain foil. However, the dramatic volume change at the foil surface during cycling and the high reactivity of Li metal against organic electrolytes can easily cause formation of dendrites, leading to poor Coulombic efficiency and eventual cell failure. Many attempts have been made to improve the cycling efficiency and stability; however, further efforts are still needed in terms of materials processing, cell assembly and cost effectiveness.

Transforming the electrode structure from a plain foil to stacked microparticles has several advantages: (1) the porous structure enhances the active surface area, thereby decreasing the local current density; (2) the cavities can alleviate the volume change during cycling; (3) the powder form allows for a well-controlled mass loading, which is essential when balancing mass of cathode and anode during cell assembly; (4) the powder form also allows easy blending with functional additives (e.g., polymer binder and conductive filler) to further improve cell performance; (5) finally, microparticles are usually easier to prepare than nanoparticles and therefore more applicable for the industrial purpose. As such, microparticle-based material systems have been successfully used in many challenging electrode systems, with the silicon particle-based anode being a notable example, along with several others such as metallic magnesium anode or metallic bismuth anode. However, the pursuit of preparing metallic lithium microparticles (Li MPs) has been barely investigated and the preparation details were not fully disclosed. Commercial sources of Li MPs are not common. Therefore, it is of significant academic and industrial interest to develop a method for the large-scale and relatively safe preparation of Li MPs.

We report herein a facile top-down approach for preparing Li MPs that involves the use of a reactive polymer surfactant. Using Li MPs produced as such, a proof-of-concept Li MPs/carbon nanotube (CNT) composite anode (LMCA) was prepared. The LMCA showed clearly improved electrochemical performance vs plain Li foil anode in both symmetric cycling and full cell test.

The preparation of Li microparticles is illustrated in Scheme 1. Li foils were added into a glass vial containing a transparent...
polymer liquid that consisted of poly(ethylene glycol) monomethyl ether (mPEG, MW = 750) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and heated at 180 °C. The Li foil formed smaller pieces by the chemical
etching between the hydroxy groups of mPEG and the lithium metal. The lithium metal started to melt at this temperature, and then the smaller particles formed grayish emulsion in the presence of lithium salt and end-group-lithiated PEG within 10 min with a shearing speed of 800 rpm. Here mPEG serves as a reactive surfactant and the presence of LiTFSI helps to stabilize the emulsion. The hydroxy groups of the monofunctional mPEG reacted with metallic Li, thus accelerating the melting process of the lithium metal and enabling the use of substantially lower shearing forces compared to previous reports.17,18,20,21 Due to the protecting effect of the polymer chains, no corrosion of glass vials from molten lithium was observed. Therefore, a customized mixing vessel is no longer needed. The agitation was stopped after 15 min and the mixture was allowed to cool to room temperature to form uniform colloidal dispersions. Anhydrous tetrahydrofuran (THF) was added, and the mixture was sonicated overnight. The sonication not only broke down particle aggregates but also helped to clean the surface of Li MPs by mechanically removing surface impurities resulting from side reactions that occurred at high temperature. After sonication a Li MP/THF suspension was formed (Figure 1a). Since the density of lithium (0.56 g/cm³) is lower than that of THF (0.89 g/cm³), a phase separation step was adopted to extract the Li MPs. The suspension of Li MP/THF was transferred to a separatory funnel, and an extra amount of anhydrous THF was added. The suspension was kept still for 30 min and two separate layers formed (Figure 1b). The top grayish layer consisted of floating Li MPs, and the bottom layer was a solution of PEG/LiTFSI in THF with some insoluble impurities. The bottom layer was removed, whereas the upper layer was left to dry under vacuum to yield grayish powders with metallic luster, indicative of the high-purity Li. Due to the high reactivity toward ambient air, further efforts are still needed to create a transferring device for quantifying the surface purity of the Li MPs. Figure 1c shows 1.5 g of prepared Li MP contained in a 20 mL glass vials. Interestingly, the Li MP cannot form compact packing, and only 1.5 g of Li MP filled almost half the volume of the 20 mL vial. The mono-chain-end functionality of the reactive surfactant is crucial. The as-prepared Li MP using mPEG has an approximate particle size around 30–60 μm (Figure 2a,b). In contrast, Li particles prepared by using dihydroxy PEG (Figure S1) or dimethoxy PEG (Figure S2) both showed larger particle size (even >1 mm) and much broader size distribution. This is because dihydroxy PEG can serve as a cross-linker between MP and inhibits the stirring of the mixture. For dimethoxy PEG, the lack of chemical etching resulted in a much slower and insufficient process of emulsification. A solvent-processed approach to prepare lithium MPs with polymeric reactive surfactant greatly reduced the requirement for specialized instruments, making the preparation significantly easier and safer as compared to previously reported approaches.

A proof-of-concept LMCA was prepared. Because of the powder form of Li MPs, the mass loading and fabrication of electrode could be easily controlled. 80 wt % Li MP was precisely weighed and evenly mixed with 20 wt % CNT in a DAC-150 Speedmixer. The mixed powder was then pressed into a pellet with a thickness of 220 μm and a diameter of 13 mm (Figure 2c,d). After mixing, CNTs were uniformly coated on the Li MP surface (Figure 2e). SEM images of the surface and cross-section of the pellet confirmed the porous internal structure of the LMCA anode (Figure 2f,g). To study the stripping/plating behavior of LMCA, two symmetric cells using either LMCA or Li foil as electrode were assembled, respectively in a 2032-type coin cell case with 1 M LiPF₆ in EC/DEC as electrolyte with a Celgard separator. Figure 3a shows the symmetric cycling of the two cells both at 0.5 mA/cm² current density, with 1 h charging/discharging times. Under this current density, the initial voltage of LMCA cell was 40 mV, while that of Li foil cell was over 160 mV. This was in agreement with the impedance spectra of the two cells measured before cycling (Figure 3b): the LMCA cell showed much lower resistance, as suggested by the smaller semicircle in the high-frequency range. During long-term charge/discharge cycle testing, the LMCA cell showed a highly stable and consistent voltage profile for the first 260 h. Insets in Figure 3a show the enlarged voltage profile of LMCA cell at hour 50 and hour 250 during the test. At both points, the overpotential was 40 mV, identical to the initial value. The cell slightly polarized by 2–3 mV after 300 h. In contrast, the lithium foil anode cell has an initial overpotential of 120 mV. The voltage profile was also much more asymmetric and spiky. The voltage increased to as high as 200 mV after 130 h. The cell eventually shorted after 130 h, likely due to internal shorts in the form of Li dendrites. The improved cycling stability is also confirmed by impedance spectra measured after 100 h of cycling. For the Li foil cell, the interface resistance increased by almost 100 Ω cm² while the LMCA cell increased only 5 Ω cm² (Figure 3c). This higher cycling stability of LMCA is due to two factors: (1) the 3D porous internal structure of LMCA and higher electrolyte/electrode contact area lead to lower local current density and reduced the chances of dendrite formation toward the counter-electrode direction; (2) the 3D structure ensured the charge transfer took place across the whole volume and greatly limited the local volume change during stripping/plating (Scheme 2).
that, after cycling, the porous structure was preserved but the surface became rougher. Symmetric cycling data at higher current densities (1, 2, and 3 mA/cm²) are illustrated in Figures S4 and S5, which also showed reduced overpotential in comparison with plain lithium foil. Due to the increased surface area, the contribution of side reactions of lithium with the electrolytes might increase. In order to prevent these side reactions, future work will focus on creating stable SEI at the surface of individual particles as well as introducing binding materials to prevent the detachment of dead lithium from the electrode. Also the effect of adding different conductive fillers such as commercially inexpensive carbon black, graphene, and copper powder will be investigated. Especially, due to the unique mechanical integrity, multiple forms, and lithiophilicity, it has been demonstrated the addition of graphene can help to prevent dendrite growth and stabilize scalable lithium loading and improve electrode mechanical properties. Another challenge will be to reduce the thickness of the electrode in order to improve the device energy and power density as well as to balance the anode/cathode weight. However, thinner electrodes may introduce more device design challenges as the percent of volume change experienced during charge/discharge will increase.

To further investigate functionality in a full cell, a LMCA anode pellet was paired with LiFePO₄ (LFP) cathode and compared to a lithium foil anode with the same cathode. The details of cathode preparation and cell assembly are described in the Supporting Information. Both long-term cycling and rate performance were tested. The capacity was calculated per gram of cathode. As shown in Figure 4a, at 0.5 mA/cm² current density, LMCA/LFP full cell showed 112 mAh/g discharge capacity in the first cycle and 111 mAh/g discharge capacity after 100 cycles, indicating less than 1% capacity loss after 100 cycles. The periodic change of capacity is due to the fluctuation of ambient temperature, while for Li foil/LFP full cell, only 104 mAh/g discharge capacity was achieved in the first cycle and 92 mAh/g discharge capacity after 100 cycles, equating to over 10% capacity loss. Moreover, in a rate performance test (Figure 4b), the LMCA/LFP also showed notable improvement over Li foil/LFP. The Li foil cell showed a discharge capacity of 132, 125, 105, 90, and 58 mAh/g at a rate of 0.1, 0.2, 0.5, 1, and 2 C, respectively, whereas the discharge capacity for the LMCA cell was 141, 132, 117, 100, and 76 mAh/g at 0.1, 0.2, 0.5, 1, and 2 C. Also the LMCA showed higher first cycle round trip Coulombic efficiency than lithium foil (Figure S7). The capacity difference is also supported by the voltage profile comparison at different current densities in Figure 4c,d. Compared to the Li foil/LFP full cell at all current densities, the voltage plateau of LMCA/LFP cell was lower during charge and higher during discharge, indicating that higher voltage could be harnessed in a LMCA anode than Li foil anode. These results suggest that LMCA/LFP full cell has much better cycling stability than Li foil/LFP full cell.

Figure 4. (a) Long-term cycling of LMCA/LFP full cell and Li foil/LFP full cell at 0.5 mA/cm² current density with 2.6 and 3.8 V voltage cutoff. (b) Rate capability test of LMCA/LFP full cell and Li foil/LFP full cells at different current densities with 2.6 and 3.8 V voltage cutoff. (c) Voltage profile of LMCA/LFP cell under different current densities. (d) Voltage profile of Li foil/LFP cell at different current densities. (capacity calculated per gram of cathode).
Noticeably, in the future, the cathode preparation will be optimized in order to achieve even higher specific capacity.

In conclusion, this work reports a facile method of preparation and extraction of a large amount of Li microparticles (Li MPs) by solvent processing. Compared to a previous approach, such a solvent-processed approach with reactive-surfactant is safer, much more user-friendly for typical laboratories, and can be easily reproduced. A Li powder form allows for making composite anode with functional fillers such as conductive carbon at room temperature, avoiding possible safety issues at temperature above melting point of lithium. A proof-of-concept composite anode based on Li MPs was prepared. Both symmetric cell and full cell cycling tests proved the advantages of using Li MPs-based anode as compared to a typical Li foil anode. Given both the academic and industrial interest in Li microparticles, the proposed procedure can attract great attention in the field of electrode materials and electrolytes for LMB. Furthermore, we envisioned that this methodology for preparing low melting point metallic microparticles could be extended to other alkaline metals anode systems, such as metallic sodium and potassium.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaeem.9b00107.

Materials and characterizations; experimental procedures for preparation of Li MPs; experimental procedures of electrode preparation and cell assembly; SEM images of lithium particles prepared from dihydroxy PEG and dimethoxy PEG; Coulombic efficiencies of full cells (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*(K.M.) E-mail: matyjaszewski@cmu.edu. Group page: https://www.cmu.edu/maty/matyjaszewski/; Twitter: Maty-PolymerLab.
*(J.F.W.) E-mail: whitacre@andrew.cmu.edu. Group page: http://www.andrew.cmu.edu/user/whitacre/.

ORCID
Sipei Li: 0000-0001-7659-1001
Francesca Lorandi: 0000-0001-5253-8468
Jay F. Whitacre: 0000-0002-3439-4111
Krzysztof Matyjaszewski: 0000-0003-1960-3402

**AUTHOR CONTRIBUTIONS**

L.S. and H.W. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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Due to a production error, this paper was published on the Web on March 11, 2019, with errors in the TOC/Abstract graphic, the abstract text, and keywords. The corrected version was reposted on March 13, 2019.