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Operando NMR and XRD study of chemically synthesized LiC_x oxidation in a dry room environment

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HIGHLIGHTS

- Dry-room stability of lithiated graphite for Li-ion anodes was assessed using *in situ* XRD and NMR.
- LiC_6 was found to be stable against CO_2, N_2, and O_2 gases and some lithium is stable against moisture.
- Delithiation of LiC_6 is limited by the mass transport of moisture to the particle surface.
- Chemical delithiation proceeds through a mechanism similar to electrochemical delithiation.
- Pre-lithiated graphite may be used to increase lithium loading in lithium ion batteries.

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ABSTRACT

We test the stability of pre-lithiated graphite anodes for Li-ion batteries in a dry room battery processing room. The reaction between LiC_x and laboratory air was followed using *operando* NMR and x-ray diffraction, as these methods are sensitive to change in Li stoichiometry in graphite. There is minimal reactivity between LiC_6 and N_2, CO_2 or O_2; however, LiC_6 reacts with moisture to form lithium (hydr) oxide. The reaction rate follows zero-order kinetics with respects to intercalated lithium suggesting that lithium transport through the graphite is fast. The reaction occurs by sequential formation of higher stages—LiC_{12}, then LiC_{18}, and then LiC_{24}—as the hydrolysis proceeds to the formation of Li_xOH_y and graphite end products. Slowing down the formation rate of the Li_xOH_y passivation layer stabilizes of the higher stages.

1. Introduction

Increasing the amount of Li is a known strategy for increasing performance and cycle life of rechargeable Li-ion batteries. The excess lithium is used in preparation and maintenance of the solid electrolyte interphase (SEI) formed primarily at the anode surface during cycling. Industry typically accomplishes this by increasing the amount of cathode material or using lithium-rich materials. This strategy results in a significant amount of wasted cathode material, which decreases the energy density of the battery. FMC Inc. has proposed a strategy to increase the lithium content in batteries by producing pre-lithiated anode materials [1]. However, pre-lithiation presents inherent difficulties: 1) pre-lithiated materials are only 0.1–0.2 V more positive than Li metal and therefore are highly reductive; 2) they spontaneously react with both the battery electrolyte and O_2/H_2O exothermically [2]; and 3) they produce a passivation layer of lithium carbonate and oxide which may inhibit Li-transport [3]. Confronting the processing problems of reactive pre-lithiated anodes is important for providing alternate means to improve battery performance by increasing Li loading or allowing for SEI synthesis.

Here we assess the stability of LiC_x in dry room battery processing conditions by following the reaction of LiC_x with ambient air using *operando* nuclear magnetic resonance (NMR) and x-ray diffraction (XRD). During processing, LiC_x may react with trace amounts of moisture present within the environment and the electrolyte to form an oxide-rich SEI as illustrated in Fig. 1. This work shows that while LiC_6 can be readily made, it is a moisture getter and will rapidly delithiate. The kinetics of delithiation is zero-order with respect to the Li within the graphite host; the

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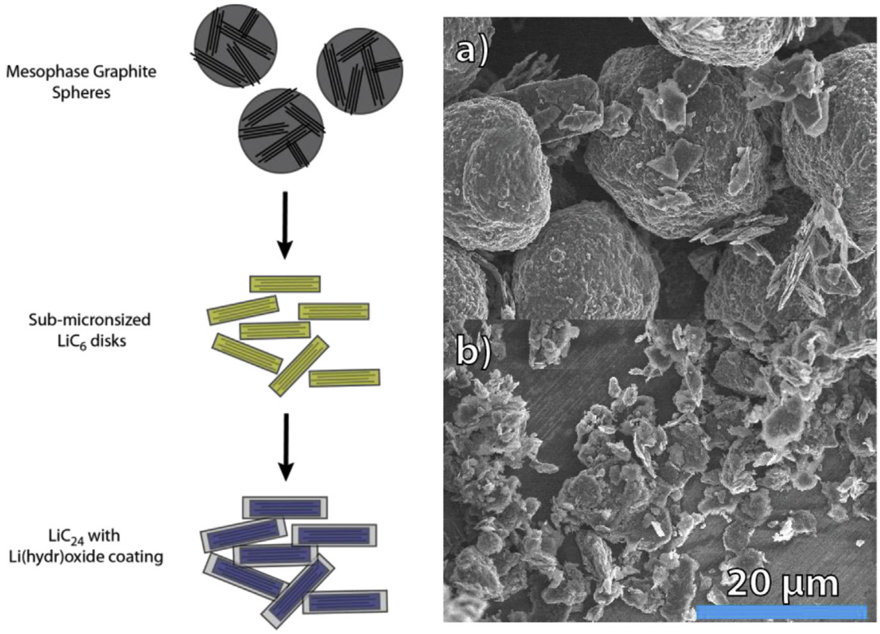

Fig. 1. Schematic of experiments (left) and SEM images (right) of annealed a) MGPA; b) ball-milled lithiated-MGPA.

rate-limiting step being the permeation of H_2O throughout the pores of the anode material. We also show that the controlled chemical delithiation proceeds in similar fashion to electrochemical delithiation, although it is irreversible. A passivating layer of lithium (hydr)oxide forms during the reaction which protects higher stages of lithiated graphite for over 24 h. Therefore, controlled exposure to moisture or organic solvents after synthesis may allow for safe handling of pre-lithiated anode materials for Li-ion battery processing.

This system is also a model for the study of chemical delithiation. We show that rapid reordering of the high stages of intercalated Li proceeds through mobile layers, *i.e.* defects or lacunar layers. Therefore the classic model of Daumas and Herold [4] is in agreement with our XRD and NMR data and recent *operando* electrochemical transmission electron microscopy (ec-TEM) results from Regan et al. [5]. Lastly, we discuss delithiation mechanism and suggest possible reasons for the chemical stability of higher stage LiC_x.

2. Experimental section

2.1. Synthesis of LiC_x

The carbon source was a mesophase graphite (MGP-A, Pred Materials) annealed under Ar(g) for 3 h at 500 °C and immediately transferred into an Ar atmosphere glovebox. Stabilized lithium metal powder (SLMP®, FMC Lithium) was stored in the same glovebox and used as received. The MGP-A (3 g) and desired molar ratio of SMLP were added to a gas-tight high-density polyethylene container along with 10 g of dried ZrO_2 milling media (5 mm dia.). The container was then placed into a stainless steel bomb, sealed, locked into an SPEX 8000M mixer/mill, and shook vigorously for 1.5 h. Afterward, the container was brought back into the glovebox for further use.

2.2. Characterization

The graphite particles were imaged using a Hitachi-S4800 scanning electron microscope (SEM) operating at 2 kV with a probing current of 10 μA. N_2 Brunauer, Emmet, and Teller (BET) surface area measurements were performed with an Autosorb-1-C (Quantachrome Instruments) at 77 K. X-ray diffraction (XRD) samples were prepared in the glovebox by sealing powders between two 25 μm-thick Kapton® sheets using Torseal®. Measurements were made using an X'pert Pro diffractometer (PANalytic, Inc.) with Cu-K_α x-ray source operating at 45 kV and 40 mA. Scattering angles 10–100° (10–30° for time-resolved spectra) were collected in 0.02° steps with a count time of 0.4 s per step. The spectra were indexed with powder diffraction files (HighScore Plus, ICDD and COD) 96-101-1061 for graphite, 04-002-4997 for LiC_6, and 35-1046 for LiC_{12}.

^7Li NMR spectra were recorded on a 9.4T Bruker 400 Avance III NMR spectrometer operating at a ^7Li resonance frequency of 155.57 MHz. Lithium mobility is high enough at room temperature in lithiated graphites so that motional narrowing of the resonance produces ^7Li line widths on the order of 1 kHz in these nominal solids, sufficient to resolve several Knight-shifted LiC_x stages in static samples [6]. Spectra typically were acquired at room temperature (295 K) using a one pulse experiment with minimum dead times delay (5 μs), a recycle delay of 10 s, and a 90° pulse optimized for the material. Conductive samples detune the probe; therefore, careful electrical optimization of the NMR coil is required for these samples. Highly conductive materials ($LiC_{6\text{-}12}$) required on-resonance pulse times of 14–15 μs to achieve a 90° pulse; products ($LiC_{18\text{-}24}$ and LiOH) required a shorter 90° pulse, typically 10 μs. Chemical shifts were measured on samples whose height exceeds the NMR coil length by at least 1 cm and are reported with respect to an external 1 M LiCl(aq) solution: $\delta = 0$.

NMR samples were prepared in an argon-filled glovebox by sealing 0.3 g of sample in a standard 5 mm NMR tube using Torseal®. Samples sealed in this way are stable over a period of weeks. Continuous hydrolysis reactions were initiated by drilling a 1.2 mm hole through the seal and inserting the open sample tube into the bore of the NMR magnet, which could be flushed with either dry N_2 or ambient (wet) air. Step hydrolysis reactions were performed by introducing aliquots of selected gases by syringe injection into the NMR tube, displacing the argon cover gas. For these experiments the NMR tube was resealed with a tight-fitting