



Short communication

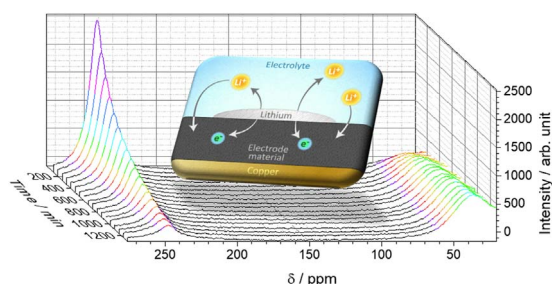
New insights into pre-lithiation kinetics of graphite anodes via nuclear magnetic resonance spectroscopy

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HIGHLIGHTS

- Solid state nuclear magnetic resonance spectroscopy study of anode pre-lithiation.
- Monitoring of reaction kinetics of pre-lithiation process of graphite with lithium.
- Observation of Li metal dissolution and formation of LiC_x species by ⁷Li NMR.
- Degree of pre-lithiation has strong impact on reaction kinetics.
- Results allow optimization of pre-lithiation times and appropriate Li metal amounts.

GRAPHICAL ABSTRACT



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ABSTRACT

Pre-lithiation of anode materials can be an effective method to compensate active lithium loss which mainly occurs in the first few cycles of a lithium ion battery (LIB), due to electrolyte decomposition and solid electrolyte interphase (SEI) formation at the surface of the anode. There are many different pre-lithiation methods, whereas pre-lithiation using metallic lithium constitutes the most convenient and widely utilized lab procedure in literature. In this work, for the first time, solid state nuclear magnetic resonance spectroscopy (NMR) is applied to monitor the reaction kinetics of the pre-lithiation process of graphite with lithium. Based on static ⁷Li NMR, we can directly observe both the dissolution of lithium metal and parallel formation of LiC_x species in the obtained NMR spectra with time. It is also shown that the degree of pre-lithiation as well as distribution of lithium metal on the electrode surface have a strong impact on the reaction kinetics of the pre-lithiation process and on the remaining amount of lithium metal. Overall, our findings are highly important for further optimization of pre-lithiation methods for LIB anode materials, both in terms of optimized pre-lithiation time and appropriate amounts of lithium metal.

1. Introduction

Rechargeable lithium ion batteries (LIBs) are widely used in all portable electronic devices and exhibit a great potential for the use in electric vehicles and for stationary storage applications. However, these

applications require improvements of the LIB in terms of energy density and costs, while keeping their safety and performance characteristics at a sufficiently high level [1–5]. The practically usable energy density of LIBs is reduced by electrolyte decomposition and the formation of the “solid electrolyte interphase” (SEI) at the surface of the anode material,

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as this process is related to the consumption of active lithium (= reversibly transferable Li^+ ions between cathode and anode) [6–10]. In particular, the active lithium losses will be high for anode materials which have a high surface area, i.e. graphitic carbons [11] having a high ratio of “non-basal-plane” surface area [12–15], or lithium storage alloys, such as tin- and silicon-based anode materials which suffer from substantial volume changes during lithiation/de-lithiation, thus, leading to ongoing re-formation of the SEI layer during cycling [16,17].

In order to compensate the active lithium loss, especially in the first cycle, various pre-lithiation methods have been developed, resulting in an increased reversible specific capacity and, consequently, in a higher energy density. These methods include: 1) the electrochemical pre-lithiation of the anode *via* a short-circuit or an external current in combination with a locally separated, thus, not the anode contacting lithium metal electrode [18,19], 2) the incorporation of a lithium reservoir [20], 3) pre-lithiation with lithium silicide inside the anode as pre-lithiation reagent [21], 4) pre-lithiation of the anode by the incorporation of lithium providing additives to the cathode like Li_5FeO_4 , Li_5ReO_6 or LiF/Co [22–24], and 5) pre-lithiation by direct contact of the anode and lithium metal. The latter technique can be realized with lithium metal foil [25,26] or stabilized lithium metal powder (SLMP) [27–34], which is to the best of our knowledge the most common method reported in literature. In order to pre-lithiate graphite with lithium metal, the latter one is typically pressed on top of the graphite anode to create intimate contact between lithium metal and graphite. Upon the addition of electrolyte, a kind of local element is formed. Electrons from the lithium metal flow into graphite and the charge will be compensated by an uptake of lithium ions from the electrolyte. Simultaneously, lithium ions from lithium metal are released into the electrolyte (Fig. 1). The major driving force of this process is the potential difference caused by different electrode potentials of graphite and lithiated graphite, respectively, vs. lithium metal. We like to point out here, that even though pre-lithiation usually also leads to formation of an SEI in parallel to the (partial) lithiation of the graphite anode material, the SEI and the SEI formation process for pre-lithiation can be different than for regular electrochemical formation, as has been discussed in Refs. [11,35].

Park et al. demonstrated rapid lithiation of graphite *via* direct contact with lithium metal by *in situ* synchrotron wide-angle X-ray scattering [36]. They could show that fully lithiated graphite is formed after ≈ 60 min. However, the experiments were done with a rather high excess of lithium, much more than the graphite could accommodate. Reaction kinetics of dissolution of lithium metal in the electrolyte and the parallel pre-lithiation of graphite will inevitably change when the amount of lithium metal is adapted to the actual capacity of graphite. Forney et al. used stabilized lithium metal powder in order to pre-

lithiate silicon/carbon nanotube anodes [31], estimating the endpoint of pre-lithiation based on voltage and impedance data, though such indirect methods merely deliver endpoints in a range of 15–20 h or 40–50 h, respectively. Indeed, solid state NMR methods in addition to magnetic resonance imaging (MRI) techniques represent powerful tools to specifically identify rather localized (e.g., at electrode surfaces, or solid/liquid interphases) or transient material specific processes including evolution of Li ion concentration gradients and lithiation of graphitic electrodes in electrochemical cells, irrespective of the local structural features [37,38]. In this work, the pre-lithiation kinetics of graphite anodes in direct contact to adapted amounts of lithium metal is investigated. Nuclear magnetic resonance (NMR) spectroscopy is applied to monitor the dissolution of lithium metal and formation of the resulting LiC_x species during the pre-lithiation process with time.

2. Experimental

2.1. Electrode preparation

The electrode paste for the free standing graphite electrodes was prepared using a composition of 70 wt% graphite (SLP30, *Imerys Graphite & Carbon*), 20 wt% of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, M_w : 400000, *Sigma-Aldrich*) as binder and 10 wt% of conductive carbon black agent C-nergy Super C65 (*Imerys Graphite & Carbon*).

First, PVdF-HFP was dissolved in acetone (*Sigma-Aldrich*). Thereafter, the plasticizer dibutyl phthalate (DBP, *Acros Organics*, purity: 99%), i.e., 30 wt% of the total mass of graphite, PVdF-HFP and Super C65, was added to the solution, followed by the conductive carbon black and graphite. The electrode paste was stirred for 4 h, and afterwards, the paste was cast on a biaxially-oriented polyethylene terephthalate foil (Mylar, *DuPont*) using an automatic film applicator at a speed of 50 mm s^{-1} in combination with a standard lab-scale doctor-blade technique. The gap of the doctor blade was set to $500 \mu\text{m}$ wet film thickness. After drying at 80°C for 15 min, the freestanding and elastic electrode foil was peeled of the foil, cut ($30\text{--}40 \times 5 \text{ mm}$) and hot pressed for 1 min (80°C , 10 tons) on a copper current collector mesh (*BENMETAL*) which was carbon coated by default in order to enhance the adhesion. Afterwards, the electrodes were immersed three times for 20 min in a bath of diethyl ether to extract the DBP. The final drying step was carried out at 120°C for 24 h under reduced pressure of 10^{-2} mbar.

2.2. Nuclear magnetic resonance spectroscopy measurements

For the analysis of pre-lithiation, lithium metal foil (*Rockwood Lithium*) or coated lithium metal powder were pressed on top of the electrodes (10 tons, 10 s). The resulting pre-lithiation degree was obtained from the corresponding relative masses of lithium and graphite (10.3 wt% Li powder, 4.4 wt% Li powder, 2.5 wt% Li powder) and the practical specific capacities of lithium and graphite. Afterwards, the electrodes were vacuum sealed in a pouch foil (Fig. S2, *supplementary data*) together with an electrolyte bag (200 μL , 1 M LiPF_6 in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 by weight)). The electrolyte was released from the electrolyte bag into the pouch foil prior to the measurement, by applying pressure (= start of the pre-lithiation process; $t = 0$). Static ^7Li NMR experiments (for more information see *supplementary data*) were performed with a Bruker AVANCE III 200 MHz spectrometer operating at a magnetic field strength of 4.7 T, corresponding to a ^7Li frequency of 77.8 MHz. All spectra were obtained at room temperature at intervals of 4096 s (512 scans, 8 s relaxation time) and externally referenced to a 1 M LiCl solution at 0 ppm. The decay of the metallic lithium metal signal was observed throughout a series of spectra, such as shown in Fig. 2.

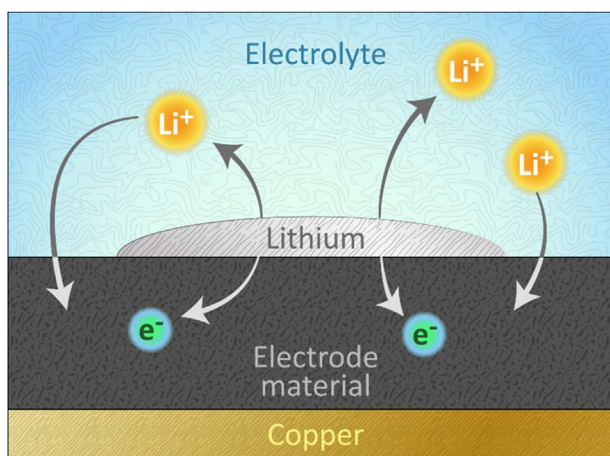


Fig. 1. Schematic illustration of the pre-lithiation process of an anode material with lithium metal.

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