Short communication

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

Florian Holtstiege\textsuperscript{a}, Richard Schmucha, Martin Winter\textsuperscript{a,b}, Gunther Brunklaus\textsuperscript{b,\ast\ast}, Tobias Placke\textsuperscript{b,\ast}

\textsuperscript{a} University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstraße 46, 48149 Münster, Germany
\textsuperscript{b} Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich, Corrensstraße 46, 48149 Münster, Germany

HIGHLIGHTS

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

GRAPHICAL ABSTRACT

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 \textsuperscript{7}Li NMR, we can directly observe both the dissolution of lithium metal and parallel formation of LiCx 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,
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 graphite 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 LiC6 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, Mw: 40000, 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 μm wet film thickness. After drying at 80 °C for 15 min, the freestanding and elastic electrode foil was peeled from the foil, cut (30 × 5 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 LiPF₆ 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.

![Figure 1](https://example.com/image.png)  
*Fig. 1. Schematic illustration of the pre-lithiation process of an anode material with lithium metal.*