SOLID-STATE NUCLEAR MAGNETIC RESONANCE USED FOR *OPERANDO* STUDIES OF NA-ION BATTERIES

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ABSTRACT

Hard carbons are a potential negative electrode for sodium-ion batteries (SIBs). Recent studies have focused on the (de)intercalation of Na ions into/from hard carbons. Compared to Li-ion, this battery is relatively new and the exact mechanism of its operation and degradation is not yet clear. In this study, the physical and electrochemical properties of half-cell nanoporous hard carbon derived from corncob prepared at 1400°C were determined by solid-state *operando* NMR spectroscopy.

Keywords: solid-state NMR, *operando*, Na-ion batteries, electrochemical mechanisms, hard carbon.

INTRODUCTION

Battery development is currently one of the most active areas of research. In this field the researchers want to understand what happens during charging and discharging, i.e. during the battery operation. Of particular interest are their mechanisms and degradation processes. Lithium-ion batteries (LIB) due to the combination of their high energy and high-power density currently remain the most desirable energy storage system for electromobility. On the other hand, sufficient energy storage systems are required for the transition from the use of fossil fuels to renewable energies and their successful integration into the power grid. Among these, sodium-ion batteries (SIB) are ideal, due to the high availability of sodium, its low cost, and suitable redox potential.[1,2] A possible negative electrode for SIB consists of hard carbons. Intercalation and deintercalation of Na ions into and from hard carbons is the focus of many recent studies. As the mentioned battery system is relatively new, the exact mechanism of its operation and degradation remains unclear.[3] In this study, we elucidated the physical and electrochemical properties of hard carbon, prepared from corncob at 1400 °C,[4] utilizing solid-state *operando* NMR spectroscopy.

While the mechanism of sodium storage in hard carbons is not yet fully understood, the galvanostatic curve (Figure 1) provides valuable insights, displaying two distinct regions. Above 0.1 V vs. Na/Na$^+$, a steep section is evident as the potential changes gradually. Below 0.1 V vs. Na/Na$^+$, the curve reaches a plateau characterized by a slower potential change. In the sloping region, capacity is linked to the adsorption of Na$^+$ ions on defect sites.[5] Meanwhile, the capacity observed in the plateau region is associated with two mechanisms: Na$^+$

intercalation between graphitic layers and filling of nanopores within the carbon structure with quasi-metallic clusters[6]. Although several storage models propose explanations for the intercalation of Na into the hard carbon, further insight is required to determine the specific mechanism of sodium intercalation and its correlation with this region of the electrochemical discharge curve.
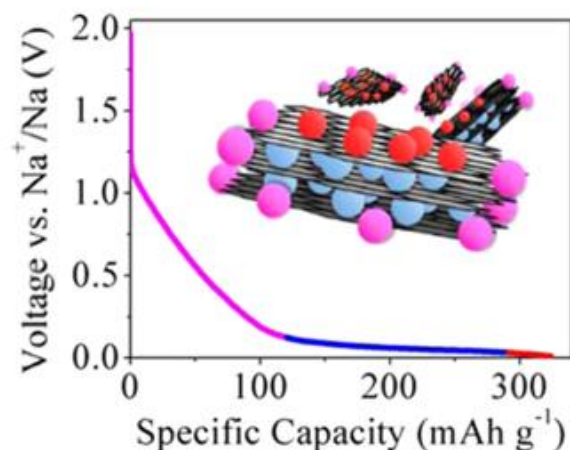

Figure 1. Electrochemistry and schematic representation of the Na-ion three-part storage mechanism.[3]

NMR spectroscopy is an extremely powerful technique, as it enables the study of local structures surrounding various pre-selected types of atoms. However, its use as an *in-situ* or *operando* technique has been relatively rare.[7] The primary obstacle arises from the intricate manipulation of samples within tightly constrained spaces and strong magnetic fields.

The study of SIB using NMR spectroscopy initially adopted an *ex-situ* approach. The samples were subjected to spinning at a magic angle (MAS) relative to the direction of the external magnetic field direction, resulting in the narrowing of the typically broad lines of the measured signal. The increased resolution facilitated the interpretation of the spectra. The batteries were then sodiated or desodiated at a certain potential and the obtained spectra thoroughly analyzed. Such approach provides information on the resulting morphologies, crystal structures, and electrochemical reaction products. However, this method can be invasive and may significantly affect the battery's state. In addition, *ex-situ* methods may not capture various metastable, intermediate, and/or short-lived phases that occur during electrochemical reactions. Therefore, recent research is focusing on *operando* measurements[8]. This technique uses non-invasive methods to observe the battery during operation, providing real-time information on dynamic structural changes and processes. We successfully designed NMR *operando* experiments and conducted measurements at the NMR center spectrometer at the National Institute of Chemistry. The study was supplemented by *ex-situ* NMR measurements. The above approaches complement each other and provide the necessary data to clarify the degradation mechanisms.

EXPERIMENTAL

Physical and chemical properties of hard carbon were determined by using XRD, SAXS, N_2 gas adsorption analysis, SEM in a previous study.[4] Sodium distribution and transport were then studied by solid-state NMR.

Solid-state *ex-situ* magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded on a 600 MHz VNMRS spectrometer (Agilent Technologies) using a 1.6 mm Triple Resonance HXY FastMAS Varian Probe. The shift axis in all the spectra was referenced using an external, secondary reference of adamantane (the ^{1}H signal was set to 1.85 ppm).

Solid-state *operando* NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer using an ATMC IN SITU NMR 400 SB Probe. The shift axis in all the spectra was referenced using an external, secondary reference of NaCl (the ^{23}Na signal was set to 7.2 ppm).

RESULTS AND DISCUSSION

Figure 2 shows the spectrum of ^{23}Na solid-state *operando* NMR performed on a half-cell system. Notably, the endpoints of sodiation and desodiation proved to be particularly informative. During the final sodiation at a potential of 5 mV vs. Na/Na$^+$, a signal emerged at 800 ppm, indicating formation of quasi-metallic clusters, characteristic of the pore-filling phase. This signal disappears upon desodiation. At full desodiation at 2 V vs. Na/Na$^+$, an additional peak begins to emerge adjacent to the metallic sodium signal, indicating the formation of dendrites on the metallic sodium surface. Figure 3 provides a schematic representation illustrating the growth of dendrites from the surface and their impact on the NMR spectrum.
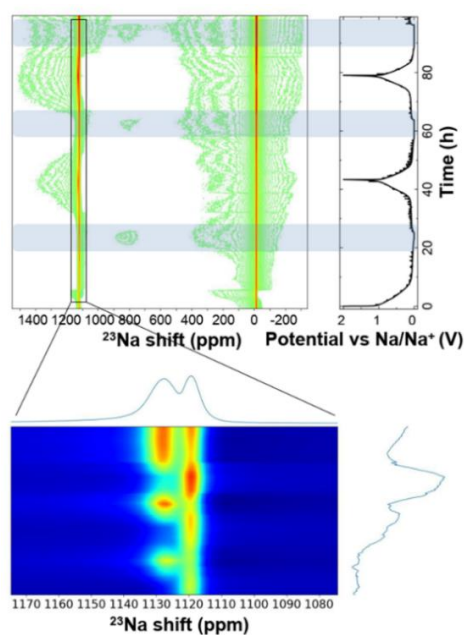

Figure 2. ^{23}Na solid-state *operando* NMR spectra of Na-HC half-cell oriented at 90° with respect to the external magnetic field. Electrochemistry measurements are added on the right. Bottom plot shows the enlarged area focusing on the signals typical of sodium metal at 1120 ppm and dendrites at 1130 ppm.
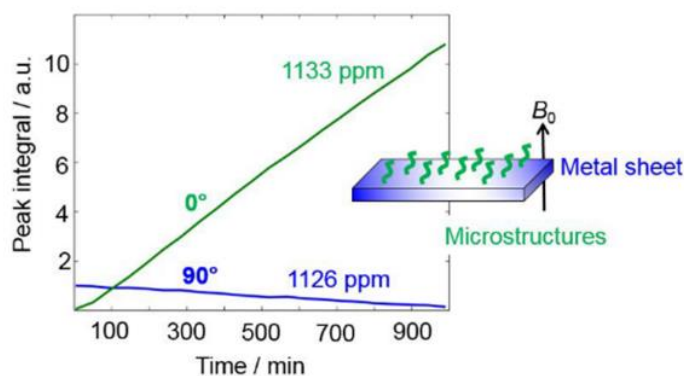
Figure 3. Peak integral variation over time for the deconvoluted Na metal signal, depicting contributions from the metal sheet (blue) and microstructure (green).[9]

CONCLUSION

Measurements of the ^{23}Na solid-state *operando* NMR spectra of hard carbon in a half-cell configuration provided information on sodium storage mechanism into the active material, leading to a shift in the NMR peak during the sodiation process and the potential formation of metal-sodium dendrites during charging. The developed *operando* approach is applicable also for systems with other porous supports.

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