

# ChemSusChem

Supporting Information

## **Electrochemical Sodium Storage in Hard Carbon Powder Electrodes Implemented in an Improved Cell Assembly: Insights from In-Situ and Ex-Situ Solid-State NMR**

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## Supplementary Information

**Structural characterization of HC powder**

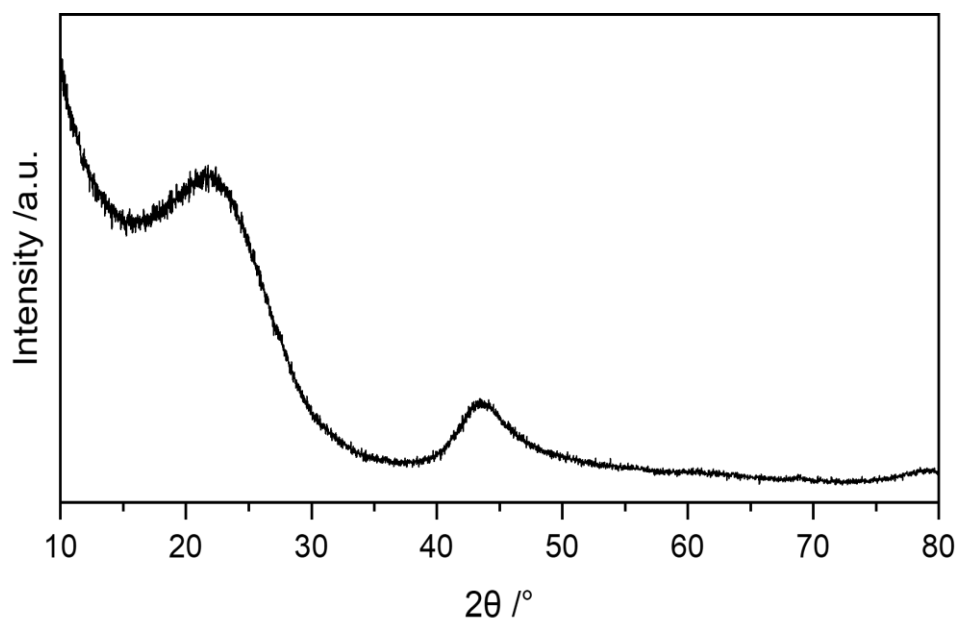


Figure S1. X-ray diffraction pattern of HC.

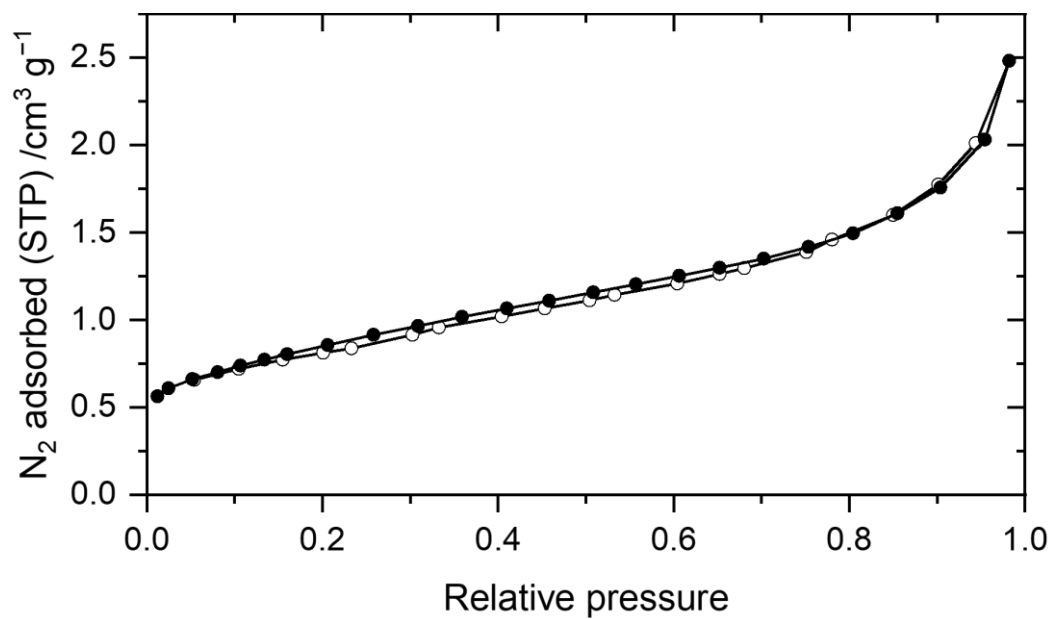


Figure S2. N<sub>2</sub> adsorption/desorption isotherm of HC at 77 K.

### ***Electrochemical characterization of HC electrode in a Swagelok-type cell***

For the electrochemical characterization in a Swagelok-type cell, the HC was fabricated into inks by grinding them together with carbon black (SuperP, Imerys) as the conductive additive. The carbon mixture was ball milled for three minutes at 50 Hz before an aqueous solution of 20 mg mL<sup>-1</sup> carboxymethylcellulose (Dupont) as the binder in the mass ratio of 90:5:5 was added. The ink was ball milled again for three minutes at 50 Hz. The ink was coated on carbon coated aluminium foil (TOB NEW ENERGY, 12 – 30 µm thickness). The electrodes were dried under vacuum at 70 °C prior to usage. The electrodes had a size of 1 mm in diameter and a thickness of 100 µm with an area loading. (2.0 – 3.0 mg/cm<sup>2</sup>). The sodiation/desodiation curve was performed in 2-electrode Swagelok-type cell on a Biologic MPG-2 potentiostat. 150 µL of a solution of 1M NaPF<sub>6</sub> in a 4:6 v/v mixture of EC and DEC was used as the electrolyte. Whatman GF/C glass fiber filters and Celgard membranes served as the separators and a thin piece of sodium acted as both, the counter and reference electrode. Sodiation/desodiation curves were recorded using voltage limitation between 2.5 and 0.002 V at 20 mA g<sup>-1</sup>. The specific capacity is calculated with reference to the electrode mass including the binder and carbon black.

In **Fehler! Verweisquelle konnte nicht gefunden werden.**, the first and sixth sodiation/desodiation cycle of the electrochemical characterization of the HC in a Swagelok-type cell is shown with a reversible capacity of 270 mAh g<sup>-1</sup> in the sixth cycle. At 20 mA g<sup>-1</sup>, the material shows typical sodiation/desodiation profiles with a dominant contribution of plateau capacity, yet including a sodium storage capacity of ~100 mAh g<sup>-1</sup> originating from "sloping" capacity.

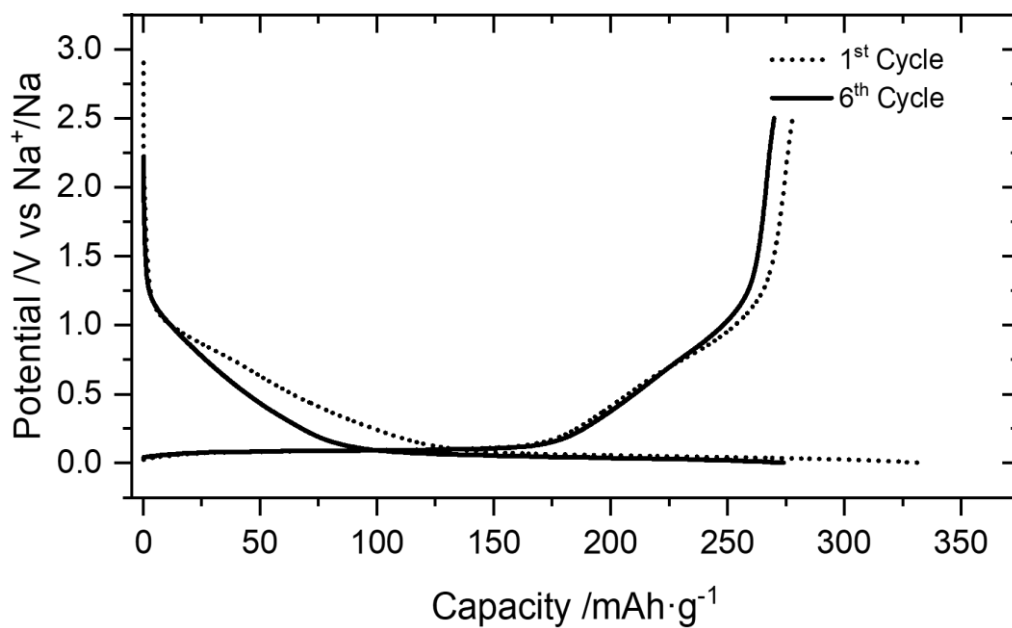


Figure S3. First and sixth sodiation/desodiation cycle of HC.

***<sup>23</sup>Na in-situ solid-state NMR and voltage profiles of Na|NaPF<sub>6</sub>|HC cells***

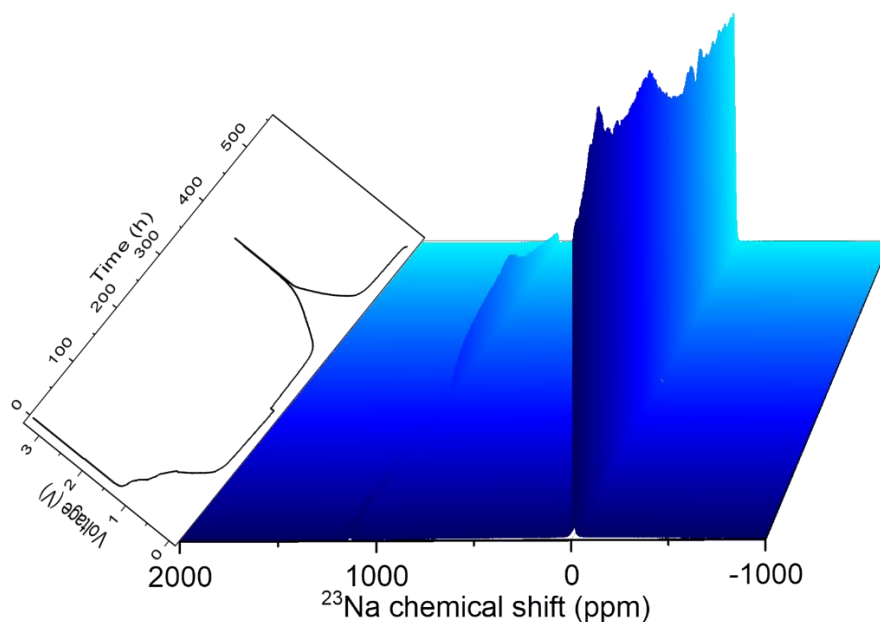


Figure S4. The voltage profile of the Na|NaPF<sub>6</sub>|HC electrochemical cell (cell **1**) and its corresponding <sup>23</sup>Na *in-situ* NMR spectra. The galvanostatic cycling was performed in the voltage window between 2.5 V and 2 mV for 22 days.

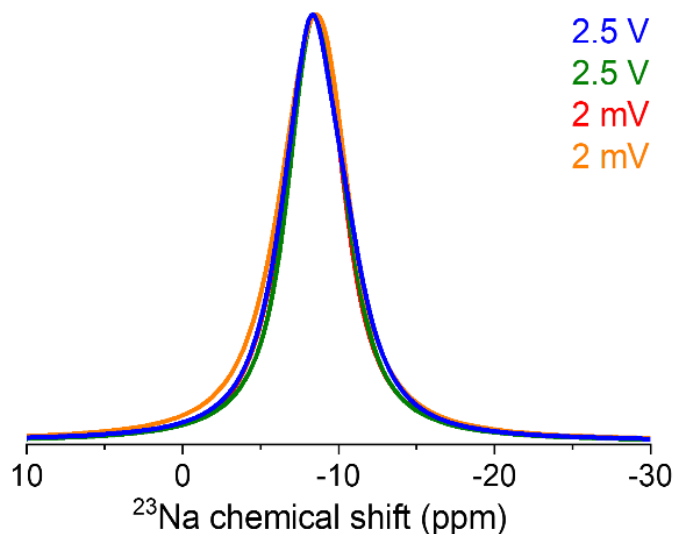


Figure S5. Extracted and normalized  $^{23}\text{Na}$  *in-situ* NMR spectra in the range between -30 and 10 ppm obtained for the Na|NaPF<sub>6</sub>|HC cell **1** at the initial state of charge at ca. 2.5 V (blue spectrum), and at the highest and at the lowest voltage of 2.5 V (green spectrum) and 2 mV (red and orange spectra).

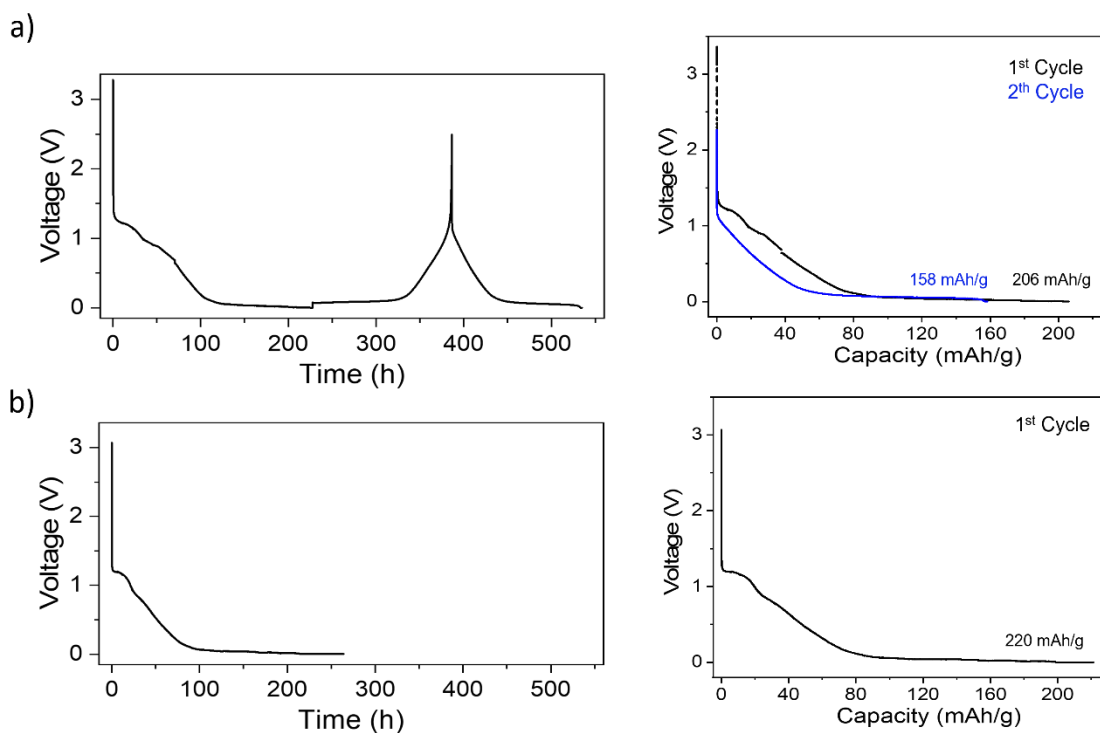


Figure S6. a) Voltage profile and capacity curves of Na|NaPF<sub>6</sub>|HC cell **1** after first sodiation (black curve) and after second sodiation cycle (blue curve). b) Voltage profile and capacity curve of Na|NaPF<sub>6</sub>|HC cell **2**.

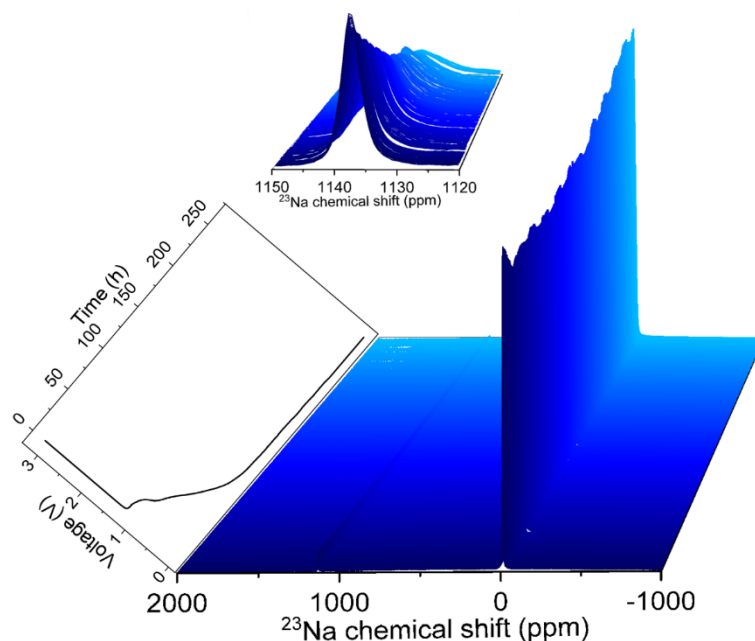


Figure S7. The voltage profile of Na|NaPF<sub>6</sub>|HC electrochemical cell (cell **2**) and its corresponding <sup>23</sup>Na *in-situ* NMR spectra. The cell **2** was sodiated to 2 mV for ca. 9 days and hold at the lowest voltage for 2 days achieving a capacity of 220 mAh/g. Enlarged view of <sup>23</sup>Na *in-situ* NMR spectra for sodium metal in chemical shift region between 1150 and 1120 ppm is shown to clearly observe intensity changes during cell sodiation.

### **<sup>19</sup>F *ex-situ* solid-state MAS NMR**

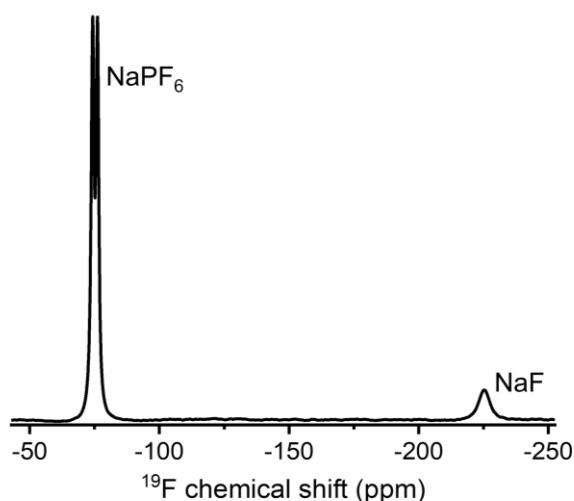


Figure S8. <sup>19</sup>F *ex-situ* MAS NMR spectrum of the HC powder electrode material of Na|NaPF<sub>6</sub>|HC cell **1** after galvanostatic cycling recorded at 18 kHz. The signal at ca. -225 ppm is attributed to NaF according to the literature<sup>[1,2]</sup> and the doublet at around -75 ppm to NaPF<sub>6</sub><sup>[3]</sup> originating from the <sup>1</sup>J (<sup>19</sup>F,<sup>31</sup>P) coupling (ca. 690 Hz).

The  $^{19}\text{F}$  *ex-situ* MAS NMR spectrum of cycled HC powder material extracted from Na|NaPF<sub>6</sub>|HC cell **1** was recorded at a 400 MHz Bruker Avance III HD spectrometer at 9 T corresponding to a frequency of 376.49 MHz for  $^{19}\text{F}$ . The spectrometer is equipped with a 3.2 mm probe allowing to spin the sample at 18 kHz. The spectrum was recorded with a background suppression sequence using composite pulses<sup>[4]</sup> implemented in the Bruker Topspin 3.6 software package. An excitation pulse of 3.10  $\mu\text{s}$  and composite pulses of 4  $\mu\text{s}$  length were employed. The repetition delay was set to 7 s and 64 scans were accumulated. The  $^{19}\text{F}$  chemical shift was referenced to CFCl<sub>3</sub> using barium fluoride (BaF<sub>2</sub>, -14.3 ppm) as external standard.<sup>[1]</sup>

### ***Skin depth effect***

The skin depth can be calculated by the following formula<sup>[5]</sup>:

$$d = \sqrt{\frac{\rho}{\pi\mu_0\mu_r\nu}}$$

where  $\rho$  is the metal electrical resistivity (47.7 n $\Omega\text{m}$  for Na),<sup>[6]</sup>  $\mu_0$  the vacuum permeability,  $\mu_r$  the relative permeability (1.0000085 for Na metal)<sup>[7]</sup> and  $\nu$  is the sodium radiation frequency of 79.38 MHz at 7 T.

From this formula, the calculated skin depth of sodium metal is around 12  $\mu\text{m}$ . Thus, the skin depth of sodium metal is much smaller than the thickness of the used sodium metal (ca. 250-300  $\mu\text{m}$ ) in our experiments. Hence, a penetration of radio waves into the bulk metal can be neglected. Since only the surface of the bulk metal is detected, where dendritic structures are deposited, the changes in intensity of the sodium metal signal can be related to the formation and elimination of dendritic structures. Note: The thickness of the dendritic microstructures has been not measured, but it is assumed to be smaller than the skin depth.



## References

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