Batteries & Supercaps

Supporting Information

SiCN Ceramics as Electrode Materials for Sodium/Sodium Ion Cells – Insights from ^{23}Na In-Situ Solid-State NMR

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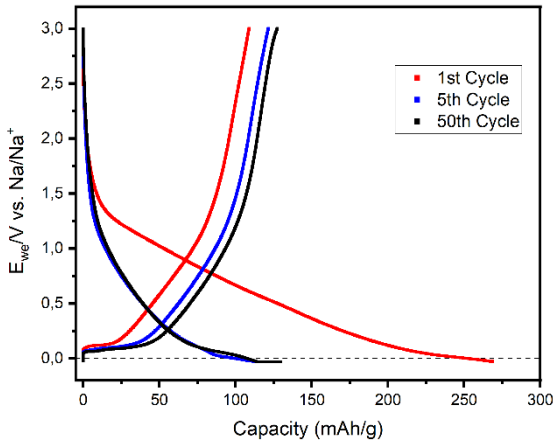
a)



b)

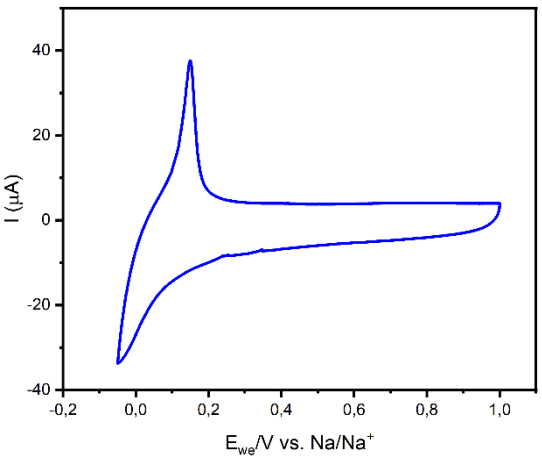


Figure S1: a) Galvanostatic charge/discharge curves of the PDC material during the 1st, 5th and 50th cycle obtained at a mass specific current of 37.2 mA g^{-1}. b) Cyclic voltammogram of the PDC material obtained in the voltage range between 1 to -0.05 V vs. Na/Na$^+$ with a rate of 20 µV/s.

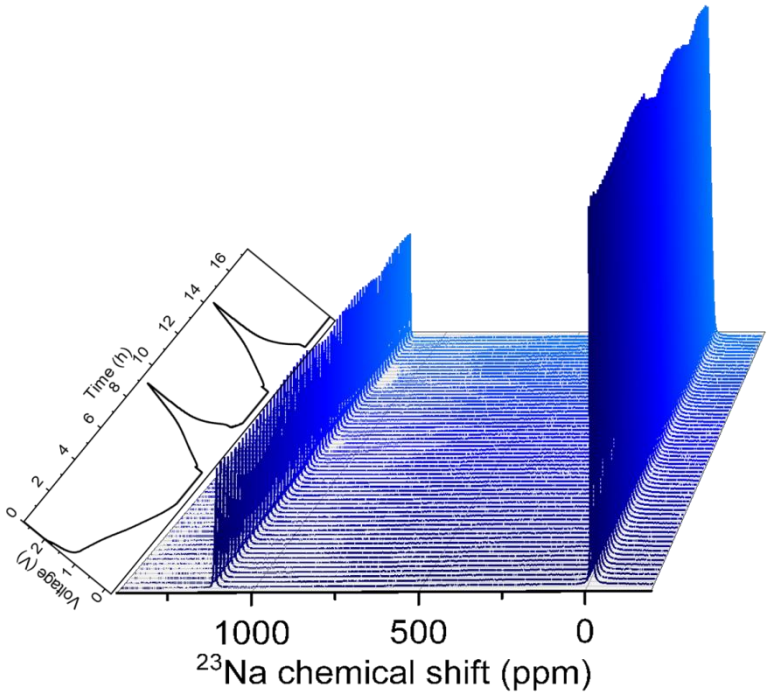


Figure S2: ^{23}Na *in-situ* NMR spectra for the Na|$NaPF_6$|SiCN electrochemical cell. The electrochemical cycling was conducted in the voltage window of -0.03 to 2.5 V applying a current of ±75 µA for 16.56 h. A 3D enlarged view of the metal and electrolyte region is presented in the main manuscript in Figure 1.

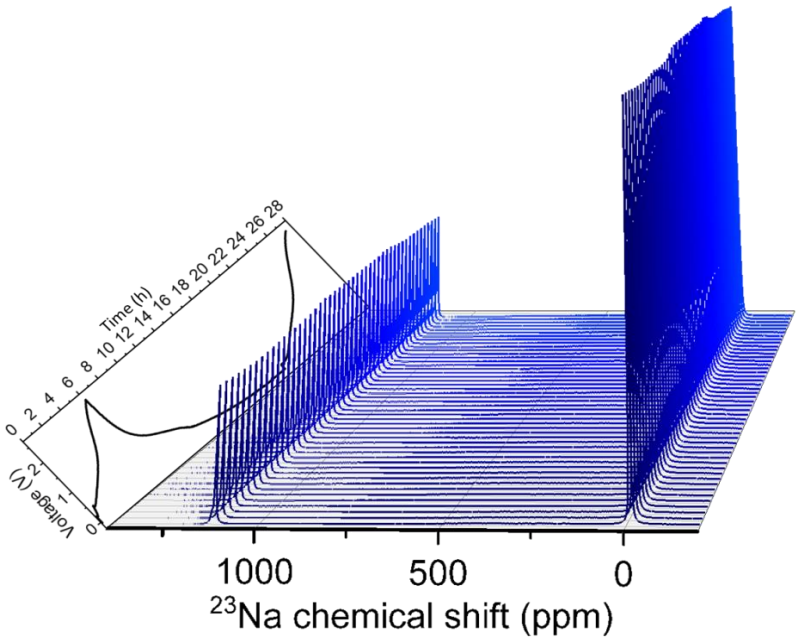


Figure S3: ^{23}Na *in-situ* NMR spectra of the Na|$NaPF_6$|SiCN cell obtained when galvanostatic cycling was performed with a current of ±20 µA at a rate of C/30 corresponding to the graphite specific capacity of 372 $mAhg^{-1}$.

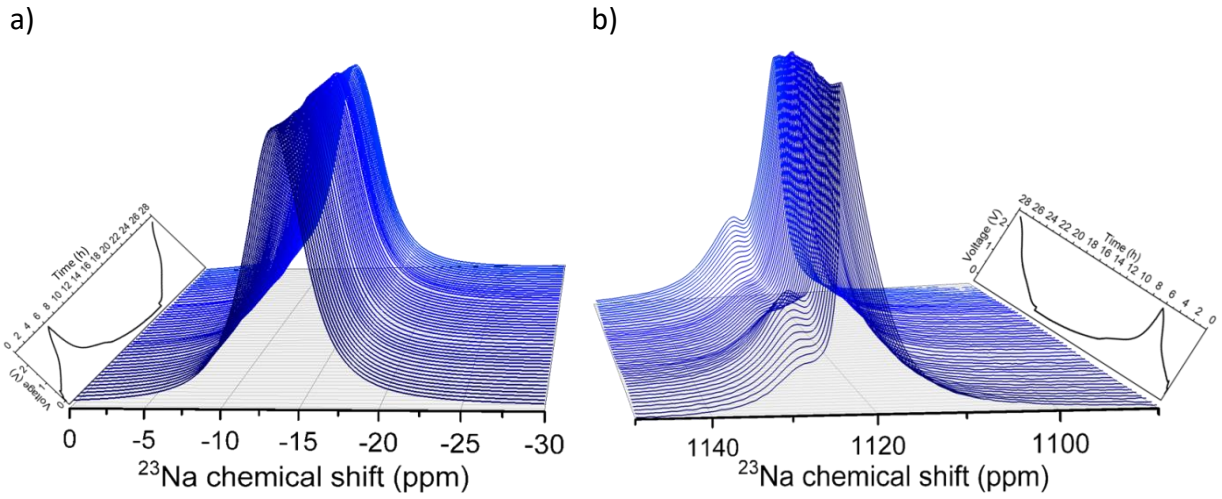


Figure S4: Enlarged 3D view of the ^{23}Na *in-situ* NMR spectra presented in Figure S3 for a) the electrolyte region (0 to -30 ppm) and b) the metal region (1150 to 1090 ppm). An increase respectively decrease of the shoulder signal at 1128 ppm during the desodiation and sodiation is visible.

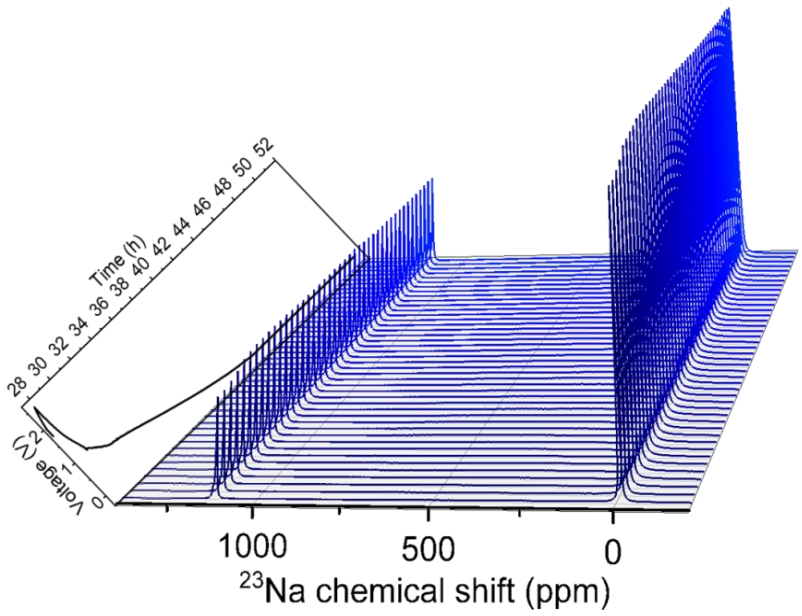
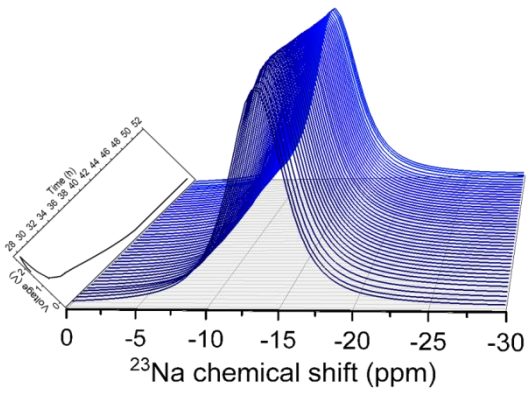


Figure S5: ^{23}Na *in-situ* NMR spectra of the Na|$NaPF_6$|SiCN cell obtained when galvanostatic performance was carried out with a current of ±20 µA at a rate of C/30 corresponding to the graphite specific capacity of 372 $mAhg^{-1}$. When the voltage minimum has been achieved, the cell was held at -0.03 V for around 10 hrs.

a)



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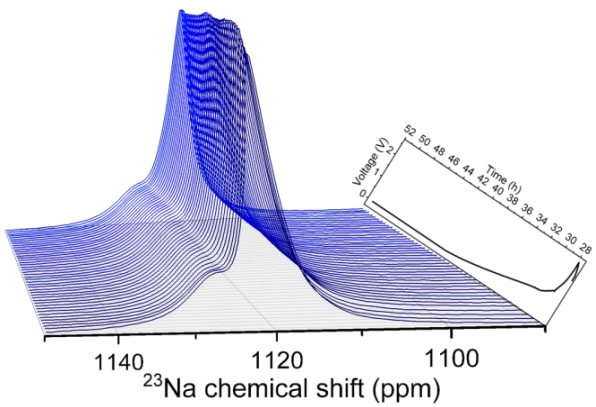
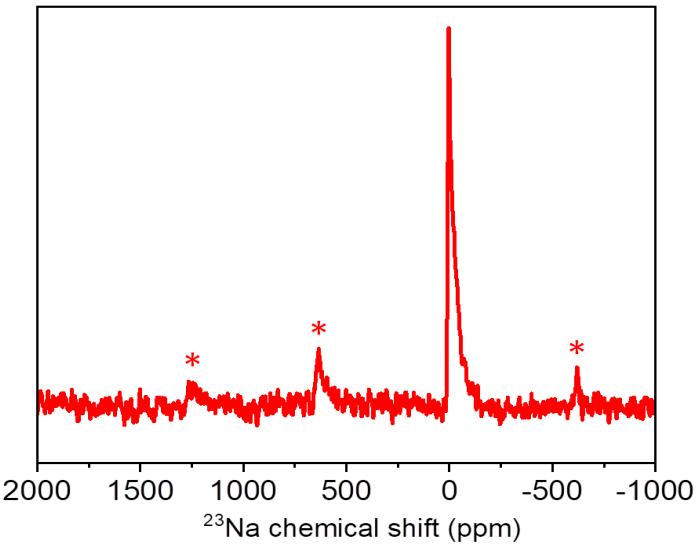
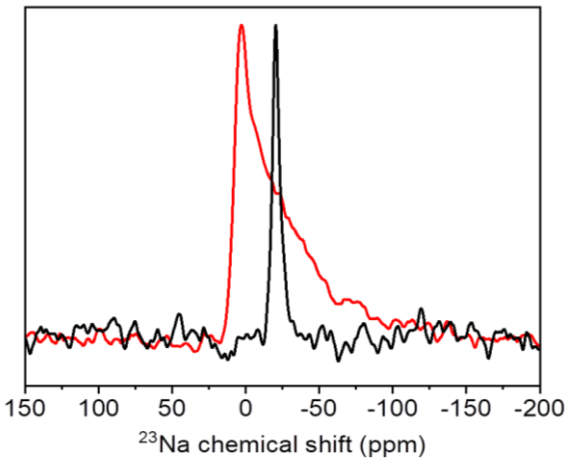


Figure S6: Enlarged 3D view of the ^{23}Na *in-situ* NMR spectra presented in Figure S5 for a) the electrolyte region (0 to -30 ppm) and b) the metal region (1150 to 1090 ppm). Along this performance, no significant changes were found in the ^{23}Na *in-situ* NMR spectra.

a)



b)



c)

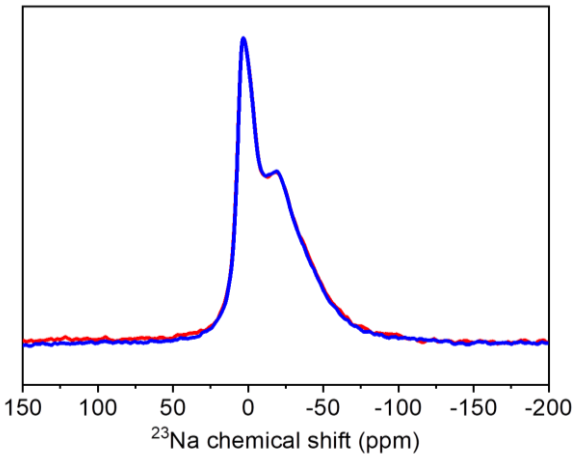
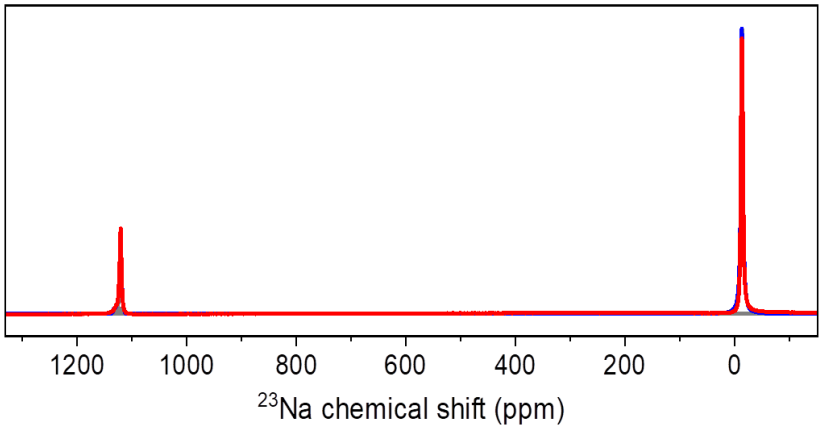


Figure S7: a) ^{23}Na *ex-situ* MAS NMR spectrum of the cycled SiCN material. The spectrum was recorded at 7 T at a spinning rate of 50 kHz with an offset of 200 ppm employing the Hahn-echo sequence. Note: Spinning sidebands are marked with asterisks. b) Zoom in of spectrum (a) (red spectrum) and of the spectrum of pristine SiCN material wetted with the electrolyte solution (black spectrum). Note: Both spectra were measured with the same acquisition parameters and are normalized to their maximum height. c) Comparison of the spectra of the cycled SiCN material recorded at 7 T at a spinning rate of 50 kHz with single pulse excitation employing short flip angles of 0.1 and 0.2 μs (blue and red spectra) and 81920 respectively 20480 scans. Note that the spectrum measured with a flip angle of 0.1 μs is scaled by a factor of 1.65 to ease the comparison.

a)



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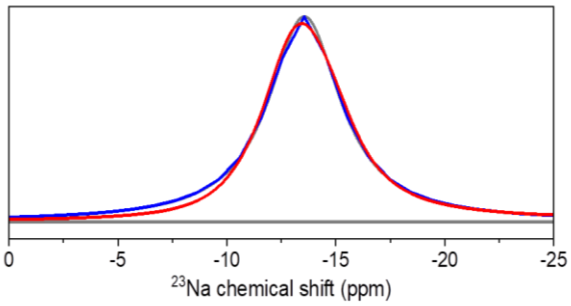

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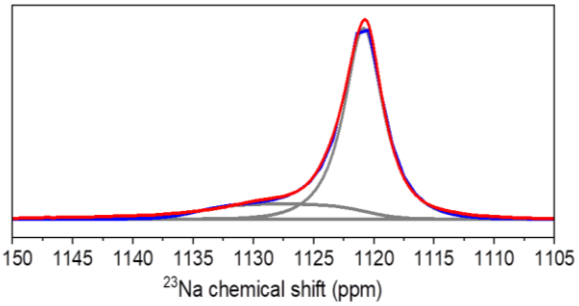

Figure S8: a) An example for the performed deconvolution of the ^{23}Na *in-situ* NMR spectra by three Gaussian/Lorentzian lines. The experimental spectrum is illustrated as red curve and the cumulative fit peak is displayed as blue curve. Enlarged view of the ^{23}Na *in-situ* NMR spectrum for b) the electrolyte region (0 to -25 ppm), and c) the metal region including the shoulder structure (1150 to 1105 ppm).

Table S1: Fit data for the ^{23}Na *in-situ* NMR spectrum shown in Figure S7.

Parameter	Chemical shift (ppm)	FWHM (ppm)	Rel. Area (%)
Fit 1	-13.55	4.00	78.83
Fit 2	1120.84	3.82	17.25
Fit 3	1127.68	13.96	3.92

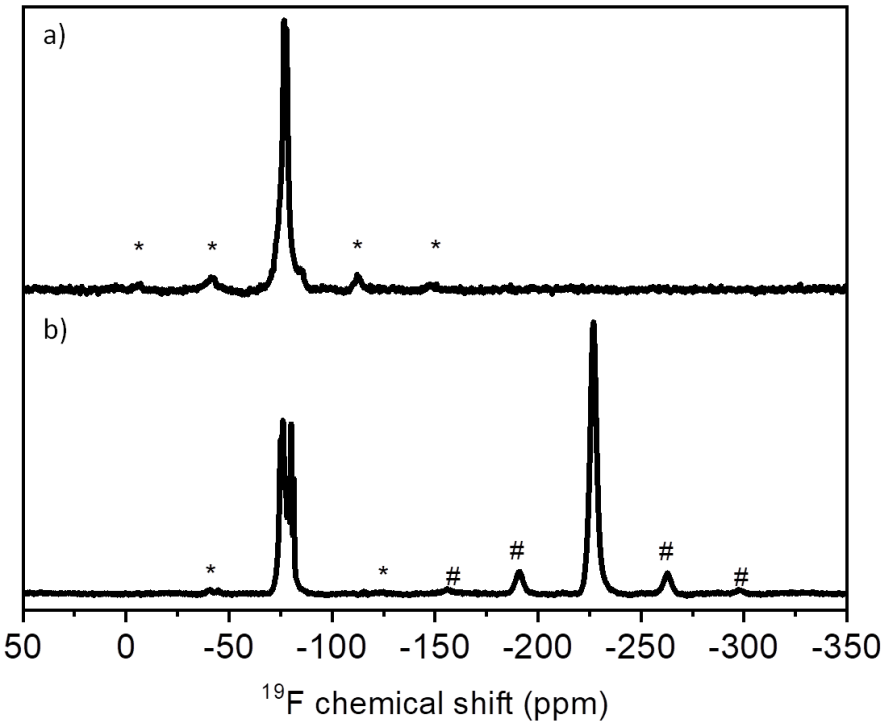

Figure S9: ^{19}F *ex-situ* MAS NMR spectra of a) the wetted SiCN with $NaPF_6$ and b) the cycled SiCN material. Spectra were recorded at 14.1 T at a spinning frequency of 20 kHz.

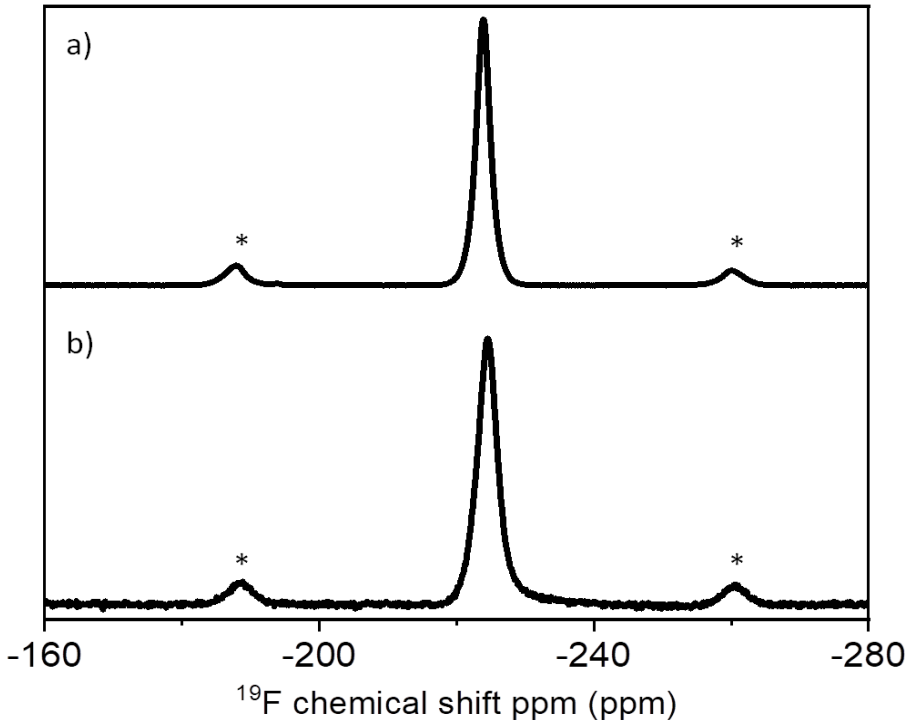

Figure S10: Enlarged view of the ^{19}F *ex-situ* MAS NMR spectra of a) NaF and b) cycled SiCN shown in S9.

The ^{19}F *ex-situ* MAS NMR spectra were acquired on a 600 MHz Bruker Avance III HD spectrometer at 14.1 T corresponding to a frequency of 564.68 MHz for ^{19}F. The measurements were performed using a 1.3 mm MAS rotor at a spinning frequency of 20 kHz and applying single pulse excitation. For the recording of the ^{19}F spectra a pulse length of 2.1 µs and a recycle delay of 3 s were set accumulating 80 scans. The ^{19}F chemical shift was referenced relative to $CFCl_3$ using the signal of the polytetrafluorethylene (PTFE) at -122.7 ppm as external reference.