Re-entrant layer reconstruction during intercalation in hafnium nitride chloride

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SUPPORTING INFORMATION

EXPERIMENTAL METHODS

Synthesis of β-HfNCl and α-HfNCl

β-HfNCl was prepared according to reference 12. A transmission electron microscopy image of the crystallites is shown in Supporting Figure S1. The particles show hexagonal platelet morphologies, and strong preferential orientation with the c axis nearly parallel to the electron beam. Electron microscopy images were obtained in a JEOL 1210 transmission electron microscope operating at 120 kV. The specimens were prepared by dispersion of the powders in n-heptane and deposition of a droplet on this suspension on a carbon coated holey film supported on an aluminum grid.

α-HfNCl was prepared by the reaction of Hf with NH_4Cl (Aldrich, 99.9 %) during 14 hours at 623°C in a sealed evacuated (10^{-5} torr) 25 cm silica tube of 10 mm diameter, followed by recrystallization during 48 hours at 517 °C by chemical vapour transport to a hot end of the tube under a temperature gradient of 100 °C.

Electrochemical experiments

Electrochemical intercalation experiments were conducted in a modified two-electrode Swagelok cell equipped with a beryllium window, using sodium slice (Aldrich, 99.9%) as the counter electrode, and were monitored with a Mac Pile potentiostat (Bio-Logic). The working electrode consisted of a powder mixture of the sample with 30 % of carbon black (Super P, MMM, Belgium) whereas two sheets of Whatman GF/D borosilicate glass fiber soaked in 1 M $NaClO_4$ (purum, Aldrich) in THF (anhydrous, Aldrich) electrolyte were used as a separator. The experiment described in the main text was performed in galvanostatic mode with an initial applied current of C/400. *In operando* diffraction was carried out using a D8-bruker diffractometer with a θ−θ geometry and Cu-Kα radiation. Representative full 2θ range X-ray diffraction patterns (from a total number of 776) are shown in Supporting Fig. S2. Lattice parameters and intensities of selected reflections were obtained from the X-ray diffraction data using the Le Bail method using the program Fullprof (Rodríguez-Carvajal, J. *Physica B* **192**, 55-69 (1993)).

Approximate phase fractions were determined from peak intensities using one well-separated (00*l*) peak for each phase. The sample texturing is not problematic because the degree of texture can be assumed to be constant for all six phases, given that the sample is static so transformed crystallites have the same orientation as their precursor. (Supporting Figure S1). The total of phases 1-6 is assumed to sum to 100% throughout.

A blank electrochemical experiment using the same amount of carbon black in the electrode confirmed that intercalation into the carbon is significant below 1.15 V (see below); for this reason the current was doubled to C/200 in the last part of the HfNCl experiment (after Q = 1.83 mA h). Intercalation into carbon also prevents reliable estimation of x in Na_xHfNCl phases after $Q \approx 0.05$ mA h. In this experiment, ~30% of the β-HfNCl sample undergoes the Phase 1 → 2 → 3 → 4 reaction sequence during the C/400 phase, and then the entire sample is transformed to the final product Phase 6 at C/200. Phase 3 persists for periods of several weeks under electrochemical reduction, but reverts when the potential is removed and attempts to isolate this phase for *ex situ* investigation were unsuccessful.

The initial reacting proportion depends on the microstructure of the working electrode; other reactions had conversions of the β-HfNCl to Phase 3 of up to 90 %. An additional in-operando X-ray diffraction electrochemical experiment at C/400 was carried out with the aim of getting further insight in the region above 1.15 V where almost all the charge is involved in reduction of HfNCl through sodium intercalation. The X-ray diffraction patterns were recorded under OCV (open circuit voltage) conditions in a D8-bruker diffractometer with a θ−θ geometry and Co-Kα radiation. The voltage vs charge profile and representative X-ray diffraction patterns are shown in Supporting Figure S5. The transitions from phases 1 to 2, 2 to 3 and 3 to 4 were observed. Phase 3 was observed as single phase for x=0.13. X-ray diffraction pattern acquisitions during consecutive cycles indicated that the intercalation reaction and the formation of these intermediate phases are reversible.

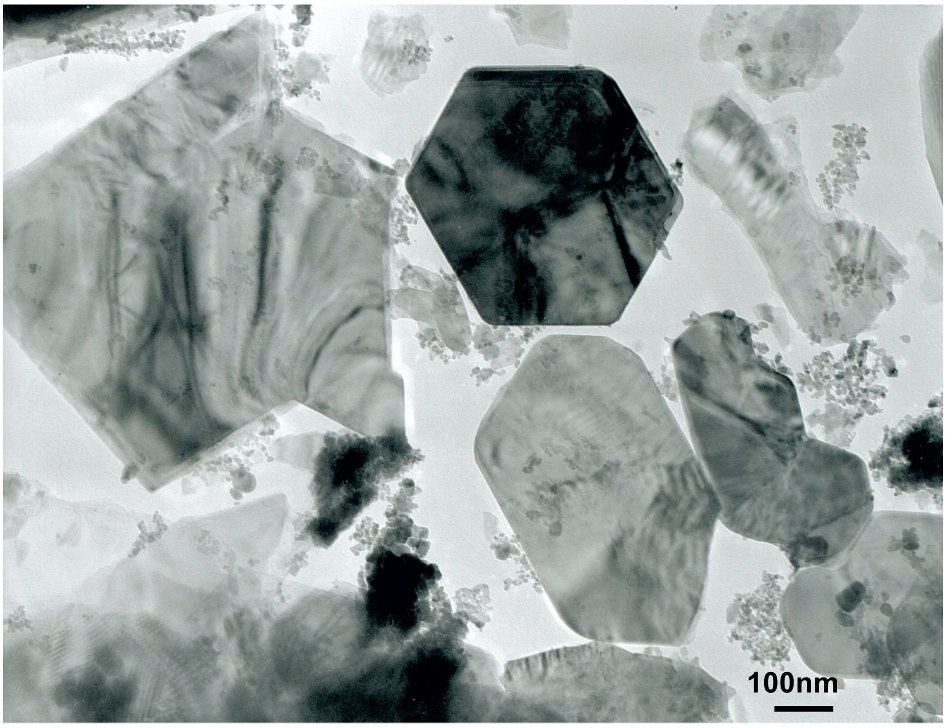
Another in-operando X-ray diffraction electrochemical experiment using similar conditions but carried out at C/10 was also performed. The X-ray diffraction patterns show the presence of the gradual growth of the stage 1 $Na_{0.5}HfNCl$ phase with interlayer spacing of 10.01 Å (Fig. 1a).

A blank electrochemical experiment at C/400 using carbon black in the electrode (4.1 mg) was performed to ascertain the extent of its reaction with sodium and the voltage at which it is observed at this rate. The voltage versus charge profile for this blank experiment is shown in Supporting Fig. S4, from which it can be deduced that this reaction mainly takes place below 1V vs Na^0-Na^+, involving a charge of 1.2 mAh down to 0.25 V vs Na^0-Na^+. Intercalation into carbon prevents reliable estimation of x in Na_xHfNCl phases after $Q \approx 0.05$ mA h.

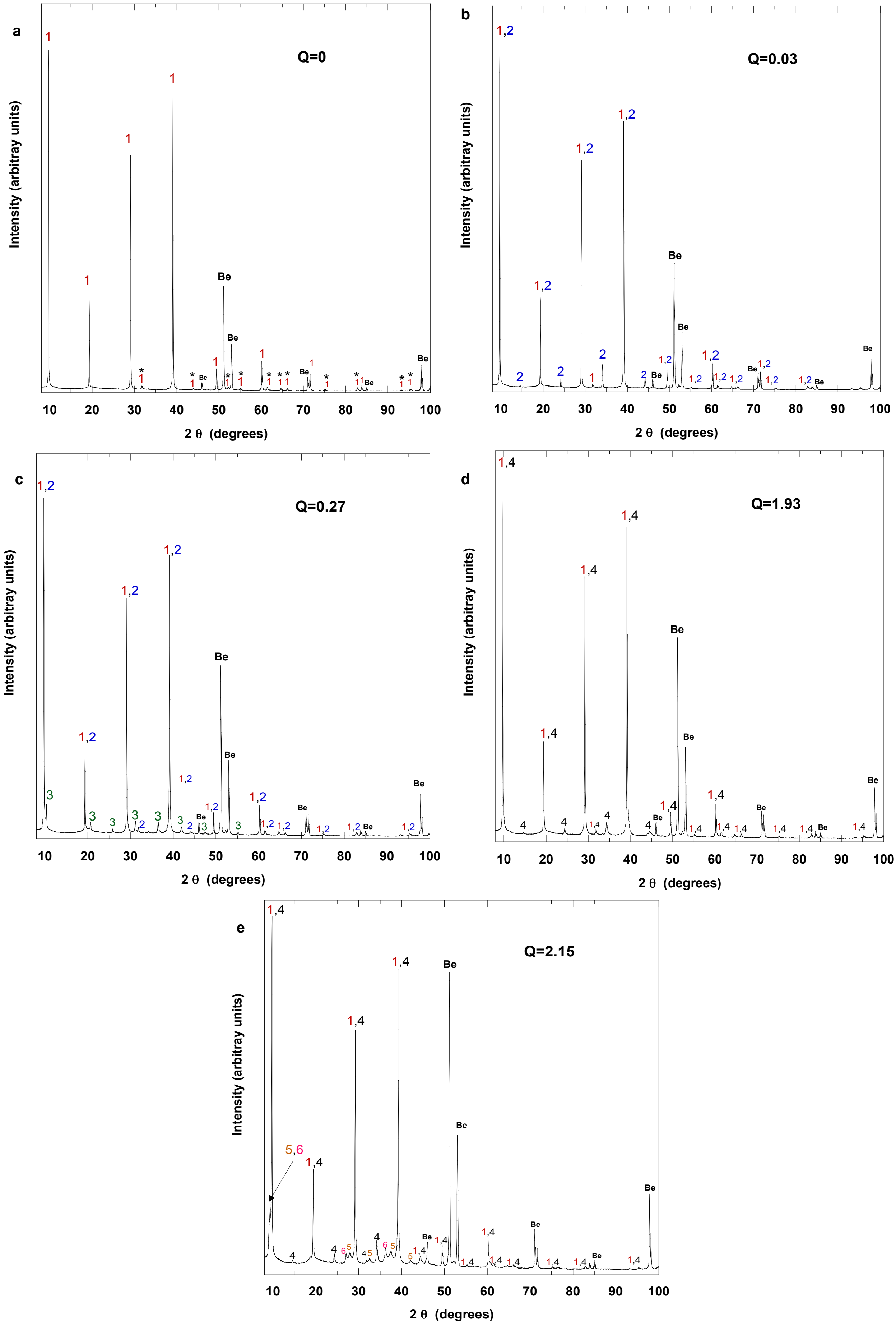
Crystal structure determination of α-HfNCl

α -HfNCl samples are not stable in ambient air and they were handled in a glove box. X-ray powder diffraction data were taken in a PANalytical X'Pert PRO MPD θ/θ powder diffractometer of 240 millimetres of radius, in a configuration of convergent beam with a focalizing mirror and a transmission geometry with a spinner glass capillary sample holder. The sample was sieved to 65 mm and mixed with glass powder before filling a capillary of diameter 0.1 mm. The radiation used was Cu Kα, with 2θ scans from 5 to 80 ° with a step size of 0.026 ° (2θ) and a measuring time of 200 seconds per step.

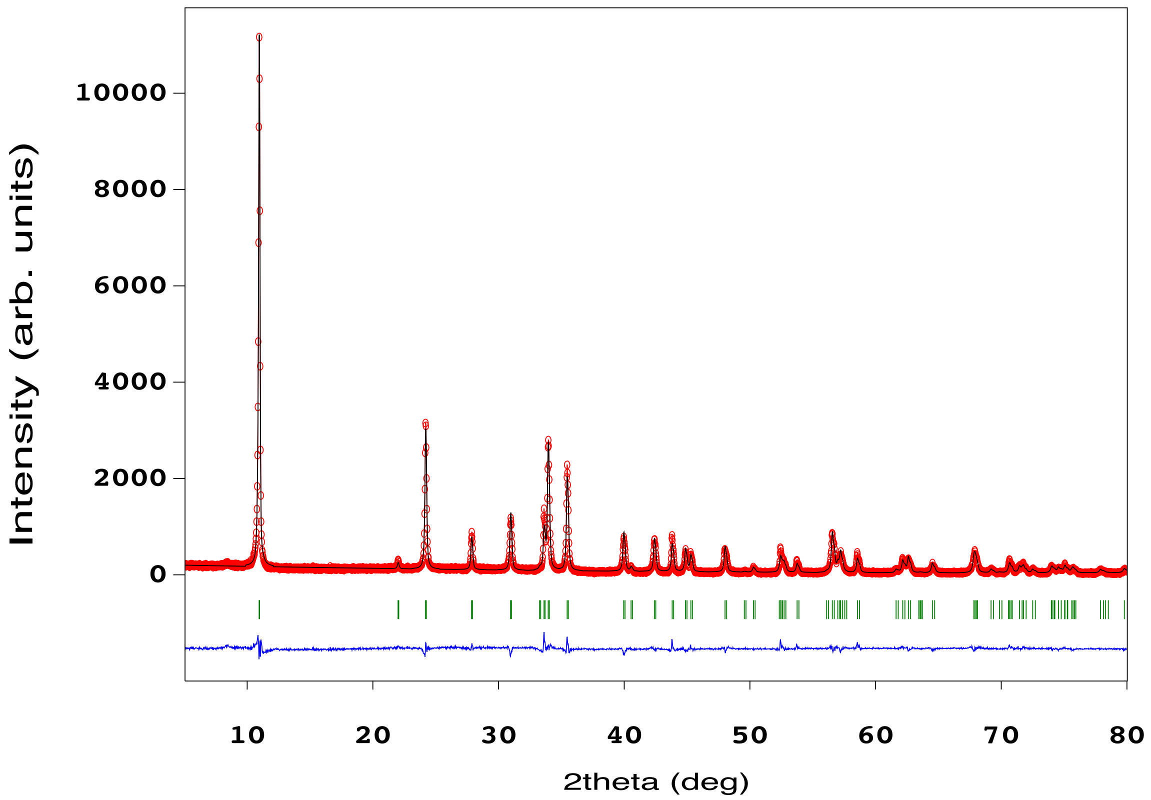
Rietveld refinements were performed with the help of Fullprof, using the atomic coordinates of isostructural α-HfNBr as initial model. The observed, calculated and difference patterns are shown in Supporting Fig. S3 and crystallographic data and details of the refinement are shown in Supporting Table S1.



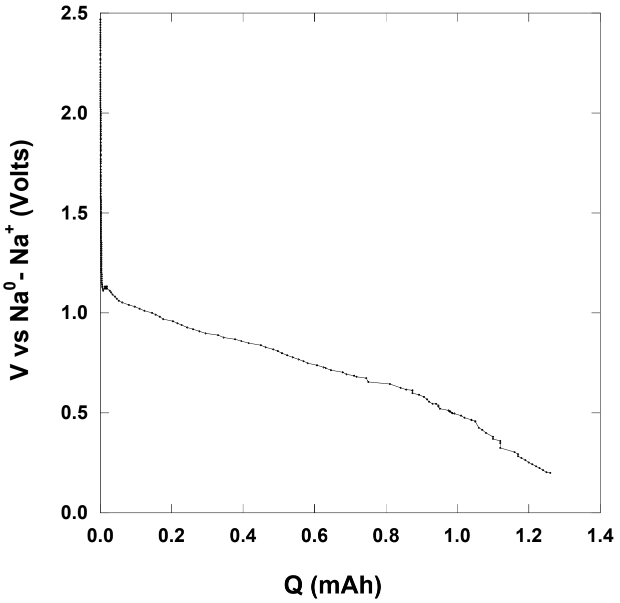
Supporting Figure S1| Transmission electron microscopy micrograph of β-HfNCl sample.



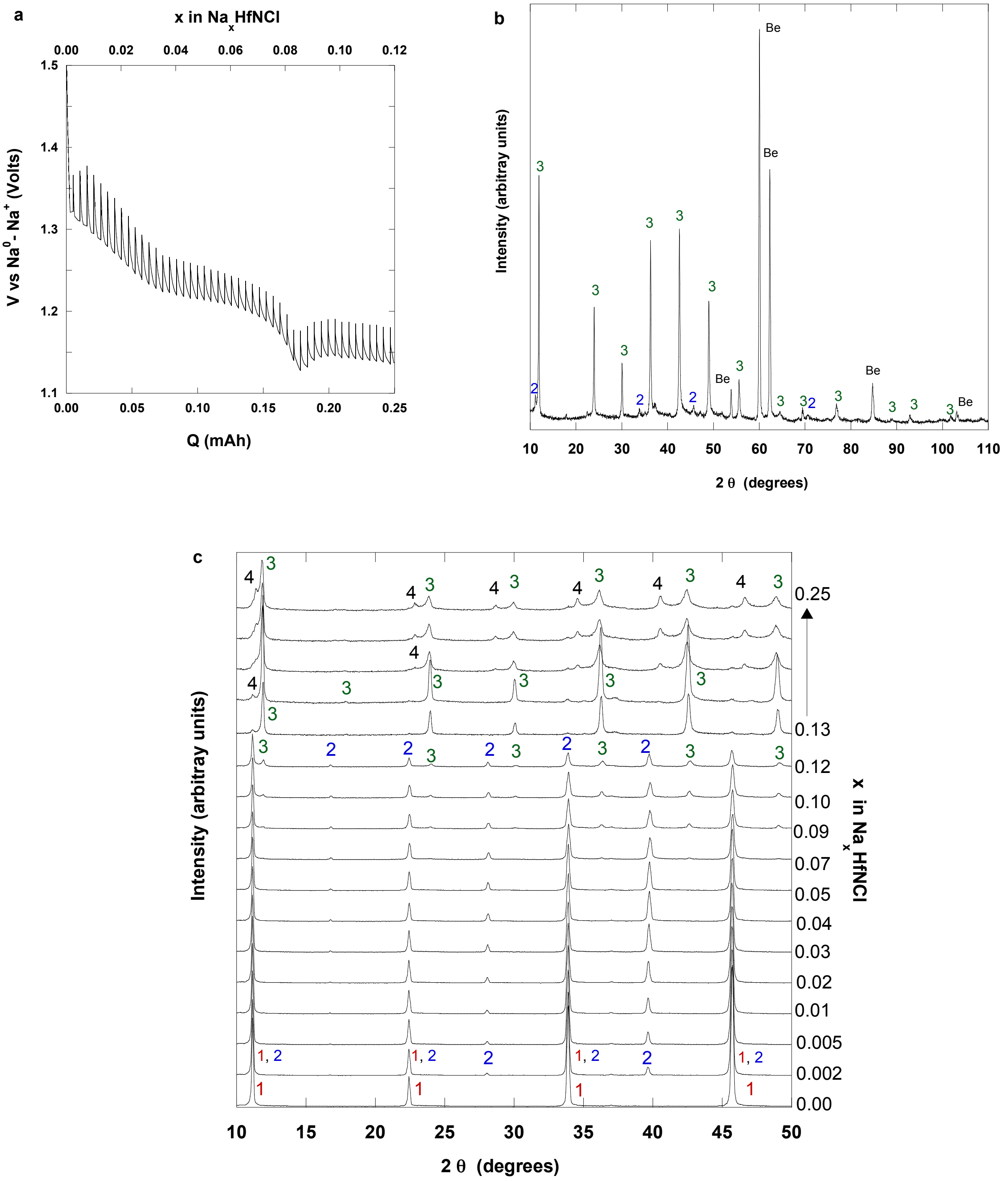
Supporting Figure S2| Powder X-ray diffraction patterns for the electrochemical intercalation experiment described in the main text taken at (a) Q = 0, (b) Q = 0.03, (c) Q=0.27, (d) Q=1.93, (e) Q=2.15. Peaks from the Be window and Na$_x$HfNCl Phases 1 to 6 are labelled. Peaks from Phase 1 (*hkl*) reflections with non-zero *h* or *k* are labelled * on (a).



Supporting Figure S3| Observed (red), calculated (black) and difference (blue) X-ray diffraction patterns for α -HfNCl.



Supporting Figure S4| Potential versus charge profile corresponding to the blank electrochemical experiment performed using only carbon black in the electrode.



Supporting Figure S5| a) Potential vs charge profile corresponding to the in operando X-ray diffraction experiment performed at C/400 above 1.15 V. b) X-ray diffraction pattern of nearly single phase 3 obtained for x=0.13. c) X-ray diffraction patterns taken under open circuit conditions at different sodium intercalation degrees.

Supporting Table S1| Crystallographic data of α-HfNCl

Crystal data

Space group	Pmmn (Nº 59), Z=2
a(Å)	4.12891(13)
b(Å)	3.48626(11)
c(Å)	8.0726(3)
Cell volume	116.201(6) Å^3
Calculated density	6.51 g/cm^3
Temperature	298 K
μ x r	1.2

Atomic coordinates and isotropic displacement parameters (in Å^2)

Atom	Wyckof site	x	y	z	B
Hf	2b	1/4	3/4	0.1092(3)	0.91(7)
Cl	2a	1/4	1/4	0.3461(10)	2.17(26)
N	2a	1/4	1/4	0.9478(30)	2.17(26)

Selected bond distances (Å) and angles (degrees)

d (Hf-N) (x2)	2.175(15)
d (Hf-N) (x2)	2.115(5)
d (Hf-Cl) (x2)	2.588(6)

Cl-Hf-Cl	84.7(2)	Cl-Hf-N (x2)	84.4(9)
Cl-Hf-N (x2)	169.1(9)	Cl-Hf-N (x4)	99.3(7)
N-Hf-N	106.5(5)	N-Hf-N (x4)	82.5(5)
N-Hf-N	154.8(2)		

N_p, N_{irefl} (c)	2856, 112
P_p, P_i, P_g (d)	8, 9, 2
R_{Bragg}, R_F, χ^2	8.49, 6.34, 3.02
R_p, R_{wp}, R_{exp} (a)	9.52, 12.6, 7.24

(a) Conventional Rietveld R-factors (R_p, R_{exp}) in %.

(b) Thermal vibrations where constrained to be isotropic and the same for the two anions and the product μ x r for the absorption correction was fixed in the refinement.

(c) N_p, N_{irefl} refer to the number of experimental points and independent reflections.

(d) P_p, P_i, P_g, refer to the number of profile, intensity-affecting and global refined parameters, respectively. The profile fitting of the data was performed with a split pseudo-Voigt function, including asymmetry and preferred orientation corrections.