

## Electronic Supplementary Information

### **Sodium chromium hexacyanoferrate as a potential cathode material for aqueous sodium-ion batteries**

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#### 1. Materials

The substrates were used as received without further purification. NaCl ( $\geq 99.5\%$ ) was purchased from Sigma-Aldrich.  $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10 \text{ H}_2\text{O}$  (99%) and  $\text{CrCl}_2$  anhydrous (97%) were purchased from Alfa Aesar.  $\text{CrCl}_2$  was stored and weighted inside the glovebox purged with nitrogen ( $\text{O}_2 < 1 \text{ ppm}$ ). Isopropanol (Sigma Aldrich) was of analytical grade and used as received. DI water ( $18.2 \text{ M}\Omega$ ) was produced by using a Milli-Q water purification system with a Q-POD.

#### 2. Analysis

##### **X-ray diffraction**

The crystal structure of the obtained materials was investigated by means of XRD technique carried out with Bruker D8 Discover diffractometer equipped with a  $\text{CuK}\alpha$  radiation source and a VÅNTEC-1 detector. Diffraction patterns were obtained in the  $15\text{-}80^\circ$   $2\theta$  range. Phase analysis was based on the matching pattern with PDF4+ (2019) database records. The parameters of the crystal structure were refined using the Rietveld method with the GSAS/EXPGUI software package.

##### **Scanning Electron Microscopy**

Scanning Electron Microscopy (SEM) images were obtained by using a FEI Teneo SEM equipped with an X-Flash silicon drift EDX detector from Bruker. SEM images and EDX data were acquired at an accelerating voltage of 10.0 kV.

### **X-Ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany). Analysis was performed using a monochromatic Al K $\alpha$  X-ray source of 24.8 W power with a beam size of 100  $\mu\text{m}$ . The spherical capacitor analyser was set at 45° take-off angle with respect to the sample surface. The pass energy was 46.95 eV yielding a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak. Curve fitting was performed using the PHI Multipak software.

### **Electrochemical characterization**

Electrochemical measurements were performed in an electrochemical glass cell inside the glovebox purged with nitrogen ( $\text{O}_2 < 1$  ppm) using a three-electrode configuration and a PGSTAT 30 potentiostat (Metrohm, CH) to control the experiments. Electrochemical tests were performed in the voltage range of 0.0 V - 1.2 V vs. Ag/AgCl (3 M KCl) reference electrode ( $E_0 = +0.226$  V vs. SHE). A Pt wire and Ag/AgCl in 3 M KCl were used as a counter and a reference electrode, respectively. An aqueous 1M NaCl solution was used as electrolyte. For the working electrode, the active material,  $\text{NaCr}[\text{Fe}(\text{CN})_6]$  powder (70 wt.%), was mixed with polyvinylidene difluoride (PVDF) binder (5 wt.%) with the addition of graphite (15 wt.%) and carbon black (10 wt.%). N-methyl-2-pyrrolidone (NMP) was added in order to obtain the proper viscosity of the pastes. The slurries were then coated on carbon felt and dried at 70 °C under nitrogen atmosphere.

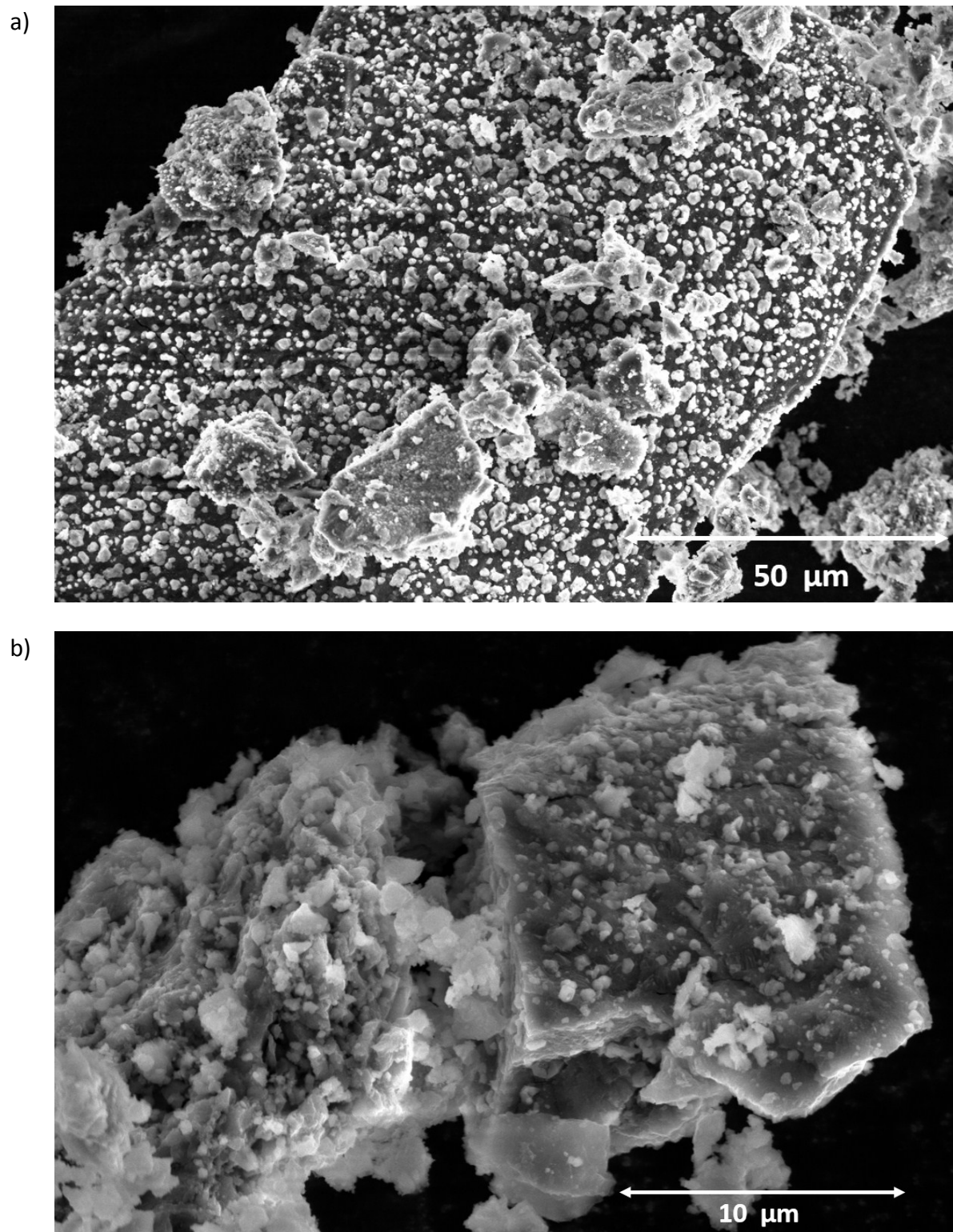


Figure S1. SEM images of NaCrHCF powder at two different magnifications.

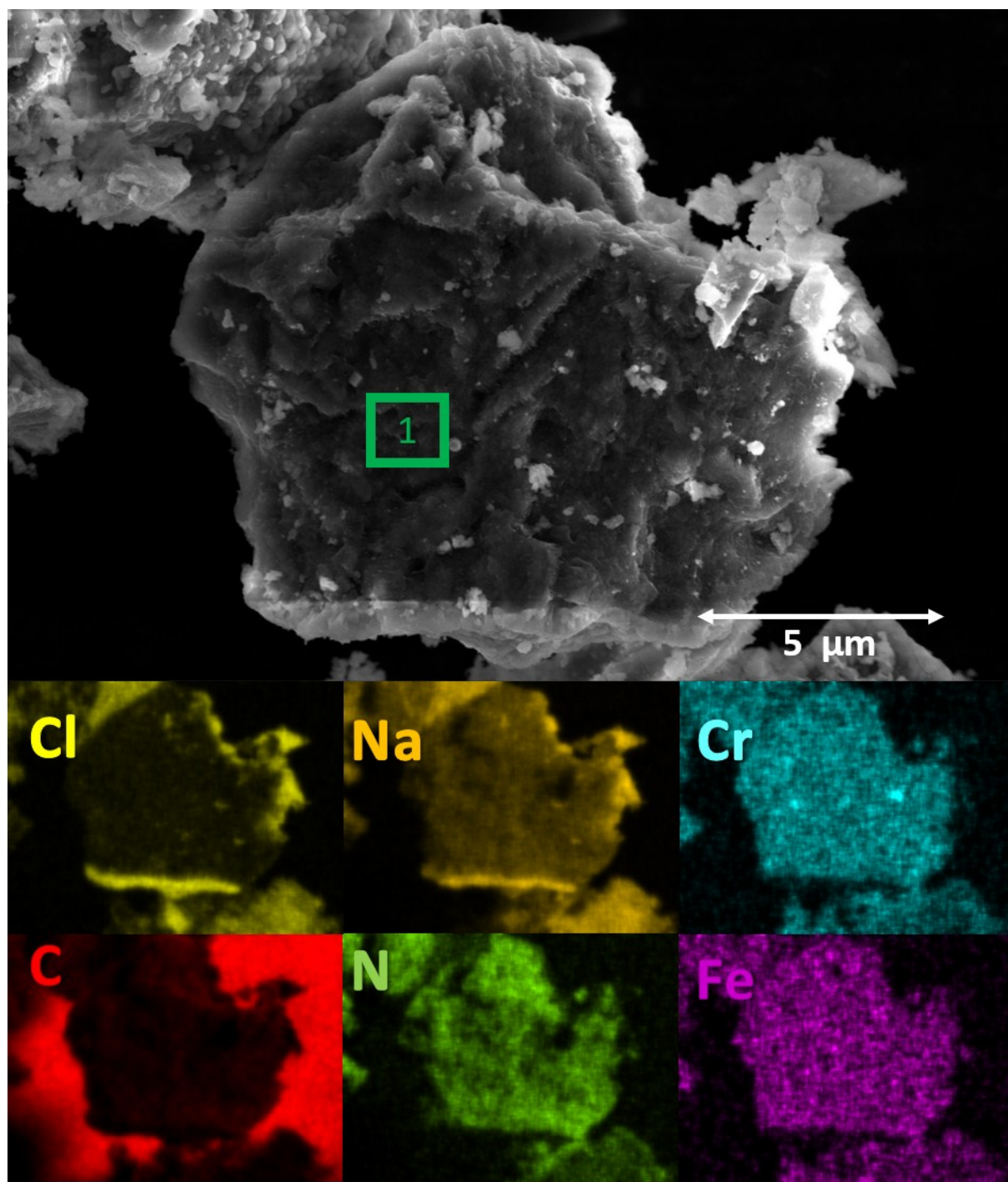


Figure S2. SEM image and EDX elemental mapping of NaCrHCF powder.

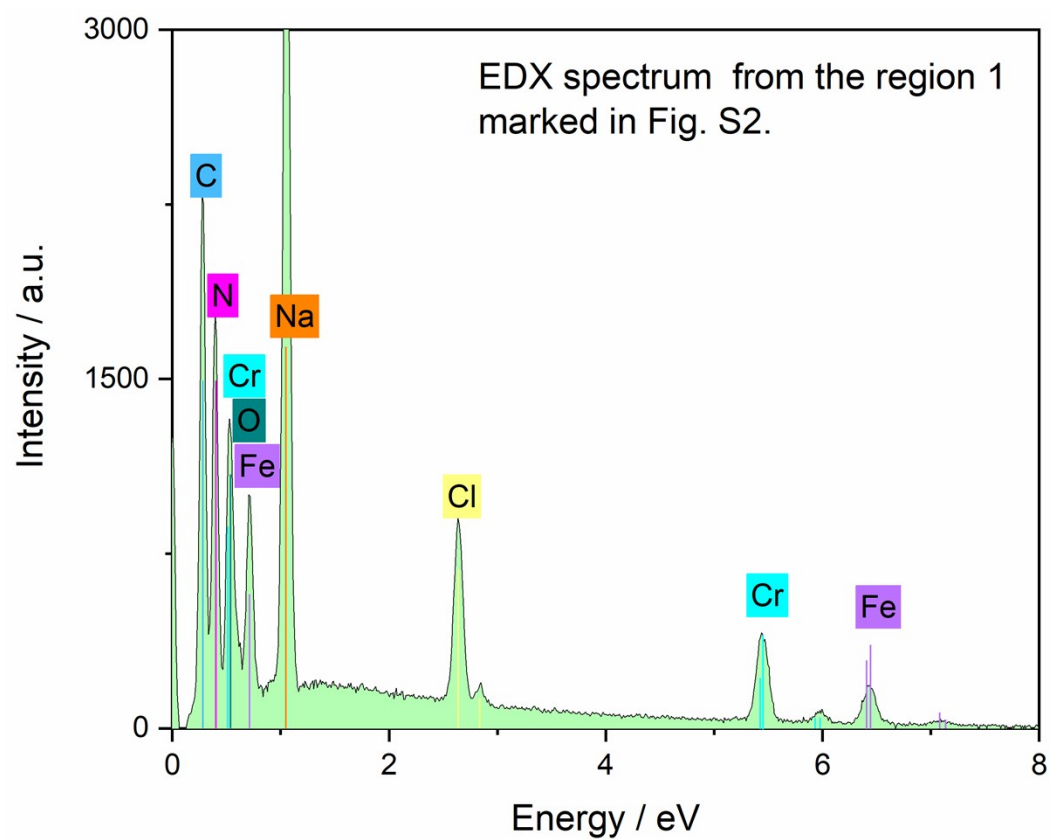
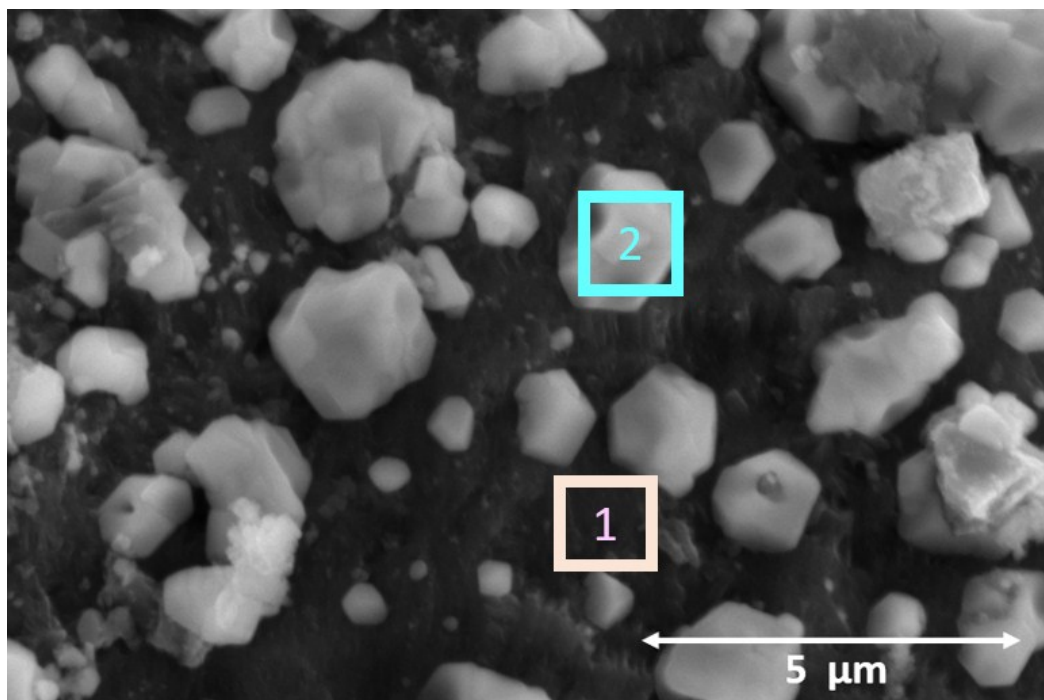


Figure S3. EDX spectrum of the pristine NaCrHCF powder from the region 1 marked in Fig. S2.

a)



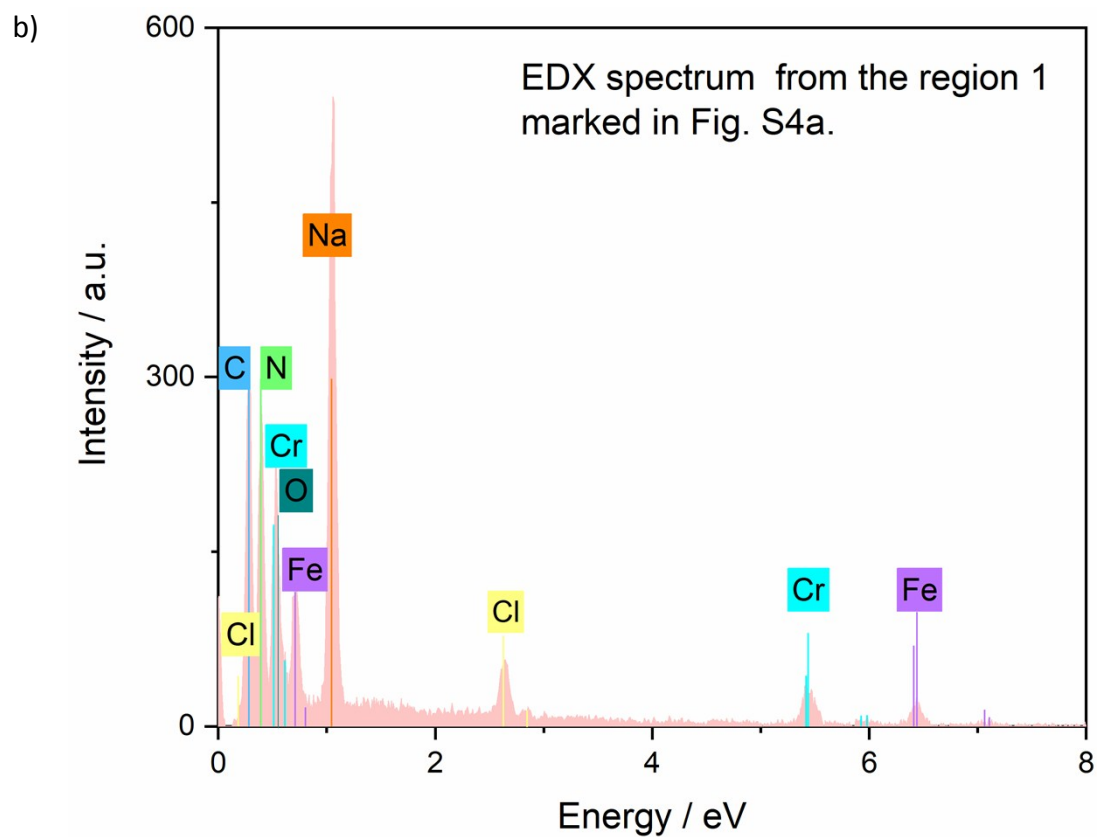


Figure S4. (a) SEM image of the as-synthesized NaCrHCF, (b) EDX spectrum of the region 1 marked in Fig. S4a.

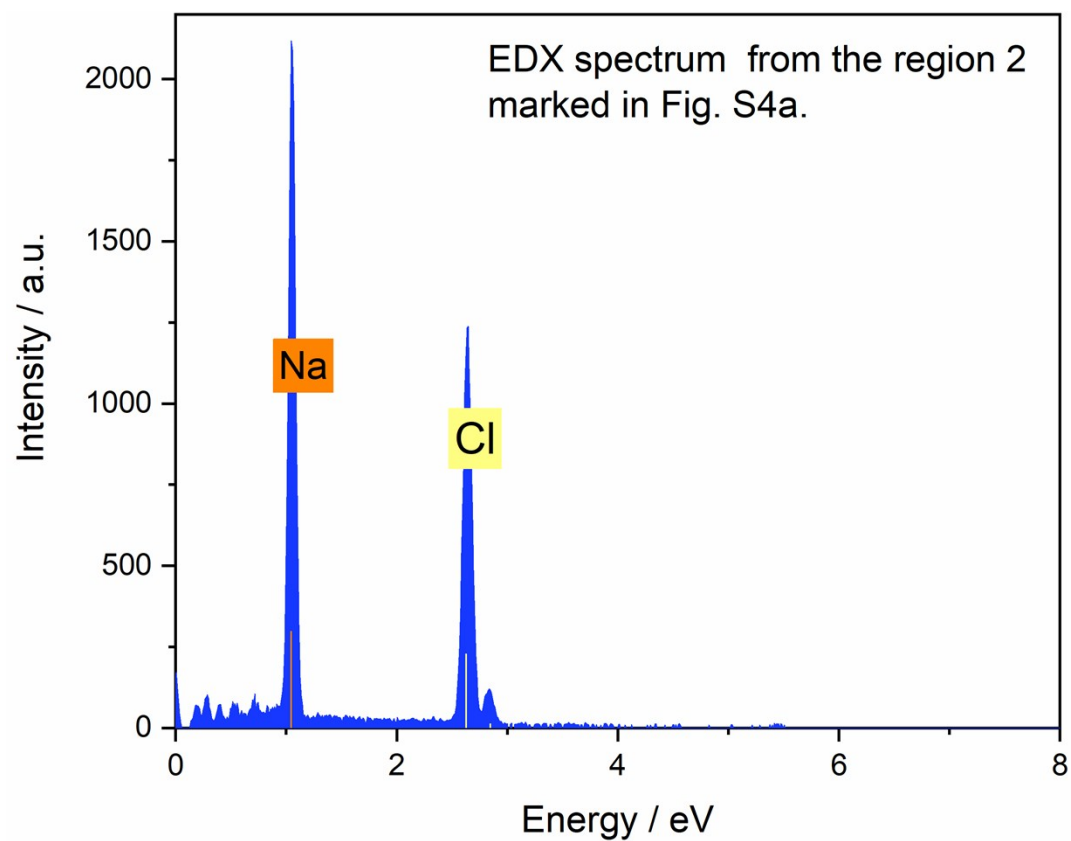


Figure S5. EDX spectrum of the pristine NaCrHCF powder from the region 2 marked in Fig. S4a.



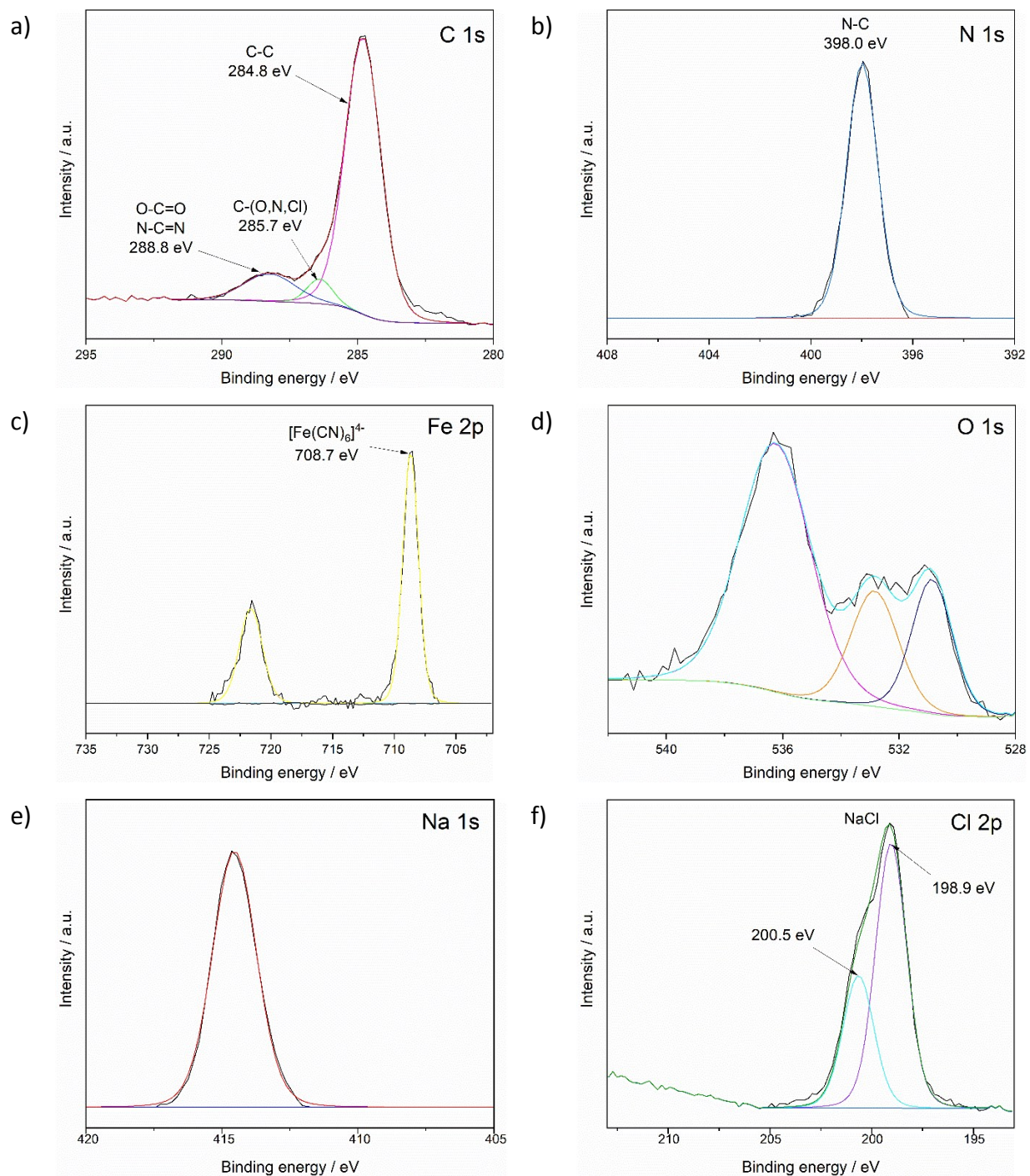


Figure S6. XPS spectra of NaCrHCF. The high-resolution core level spectra of (a) C 1s, (b) N 1s, (c) Fe 2p, (d) O 1s, (e) Na 1s and (f) Cl 2p.



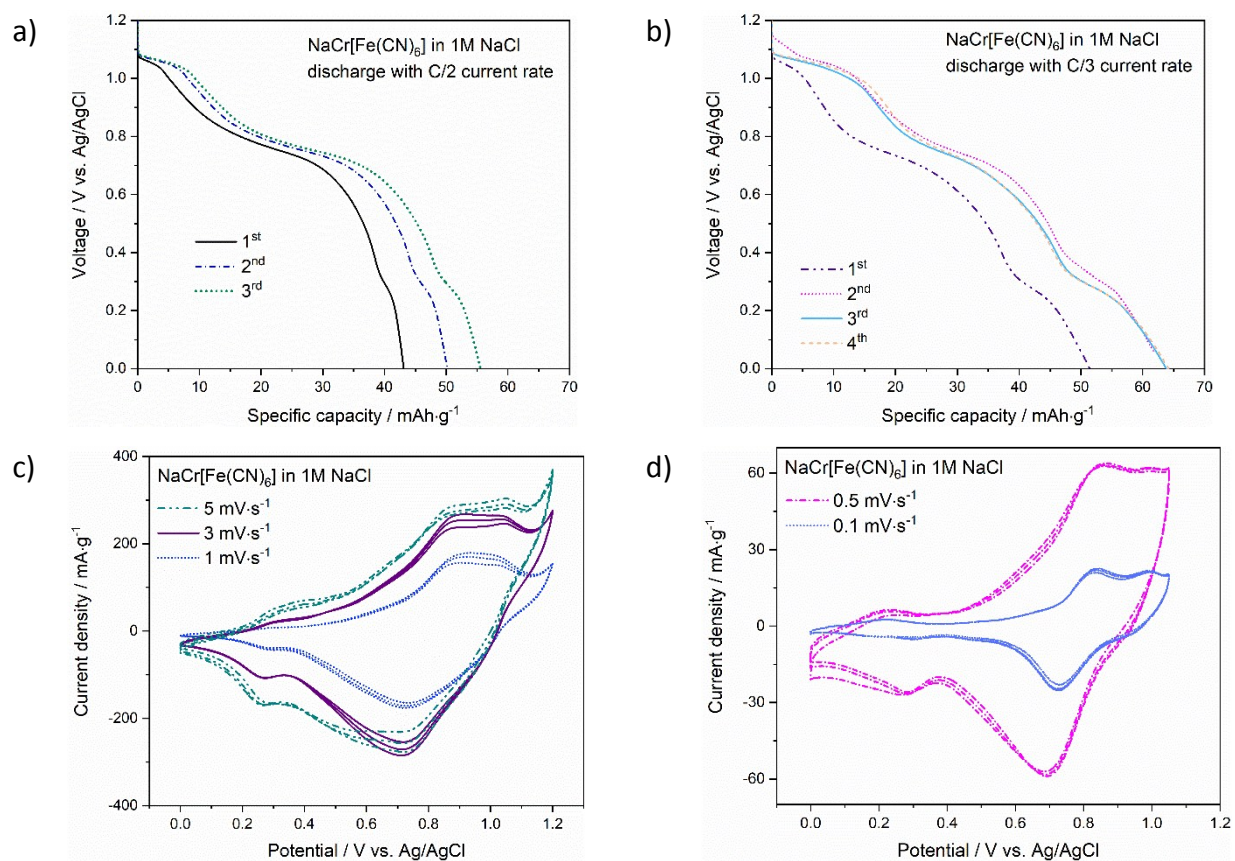


Figure S7. Electrochemical tests of NaCrHCF in aqueous 1M NaCl electrolyte: galvanostatic discharge profiles discharge curves (a) at C/2 current rate and (b) at C/3 current rate, (c) and (d) cyclic voltammograms at different scan rates.