Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


**Supporting Information**

# Selective Edge Etching to Improve the Rate Capability of Prussian Blue Analogues for Sodium Ion Batteries

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## Experimental section

### Synthesis of PBA

2 mL 6 mol $L^{-1}$ hydrogen chloride solution, 2 m mol $Na_4Fe(CN)_6 \cdot 10H_2O$ and 0.5 m mol sodium citrate were mixed in 40 mL deionized water and stirred for 5 minutes, followed by transferred into 100 mL Teflon lining and heated to 80 $^oC$ for 10 hours. Later on, the product was washed with water and ethanol for 3 times and dried in vacuum oven at 80 $^oC$. The samples were denoted as NaFe.

### Synthesis of chemical eroded PBA

In brief, 50 mg of dried NaFe powder was dispersed in 1 mL water and 1 mL hydrogen chloride solution (12 mol $L^{-1}$) by sonication for 10 minutes. Three different products were collected by contrifugation, one after 1 minutes (NaFe–1), one after 5 minutes (NaFe–5) and the third after 10 minutes (NaFe–10). Finally, the samples were dried in vacuum oven at 80 $^oC$ for 10 hours.

### Characterization

Samples were characterized with field–emission scanning electron microscopy (SEM, FEI Nova NanoSEM 50, America) and transmission electron microscopy (HRTEM, FEI Titan G2 60~300 and Philips Tecnai F20). X–ray diffraction (XRD) measurements were conducted using a D8 Advance (Bruker). X–ray diffractometer with Cu Ka radiation (λ=1.5418 Å). Thermogravimetric analysis (TGA) (Mettler Toledo, TGA/SDTA851 e) in $N_2$ at a scan rate of 10 °C $min^{-1}$ from room temperature to 600 $^oC$. UV-Vis spectra were recorded on Shimadzu UV-2450 spectrometer (Japan). Inductively coupled plasma mass spectrometry (ICP-MS) was obtained from iCAP 7400 Duo spectrometer and CHN analysis was performed on a Vario ELIII CHNOS Elementar analysator from Elementar Analysensysteme GmbH.

### Electrochemical Measurement

The cathode was prepared by mixing 80 wt% samples, 10 wt% super P carbon black and 10 wt% polyvinylidene fluorid dissolved (PVDF) in N–methyl–2–pyrrolidone to form a slurry, which was then pasted on an Al foil. Subsequently, the coated electrodes were dried in a vacuum oven at 60 $^oC$ overnight. The typical active material loading of the electrode was

0.3~0.8 mg $cm^{-2}$. CR2016–type coin cells were fabricated in a high purity argon–filled glove box. Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a Bio–logic VMP3 electrochemical workstation with a voltage range from 2.0 to 4.5 V at a scan rate of 1 mV $s^{-1}$ and in the frequency range of 100 kHz~0.1 Hz at a 10 mV amplitude referring to open circuit potential, respectively. Galvanostatic discharge and charge experiments of the coin cells were conducted using an Arbin automatic battery cycler (BT–2000) at several different rates between cut–off potentials of 2.0 and 4.5 V. Galvanostatic Intermittent Titration Technique(GITT) was performed between 2.0 and 4.5 V at current density of 20 mA $g^{-1}$. All of the electrochemical performance measurements were carried out in a two–electrode system and obtained at a constant temperature of 25 $^{o}$C by using a homemade constant temperature and humidity chamber.

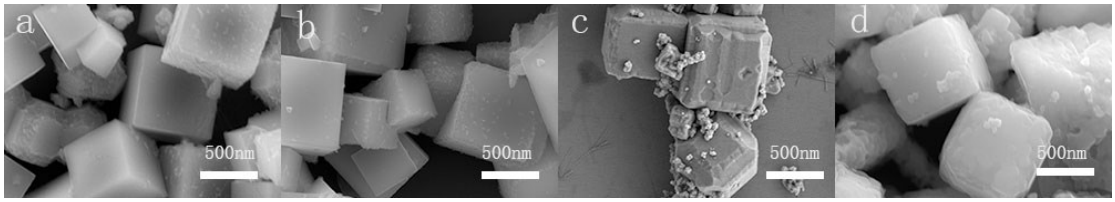


**Figure S1.** SEM images of the PBA crystals before (a) and after etching for b) 1, (c) 5, and (d) 10 minutes.

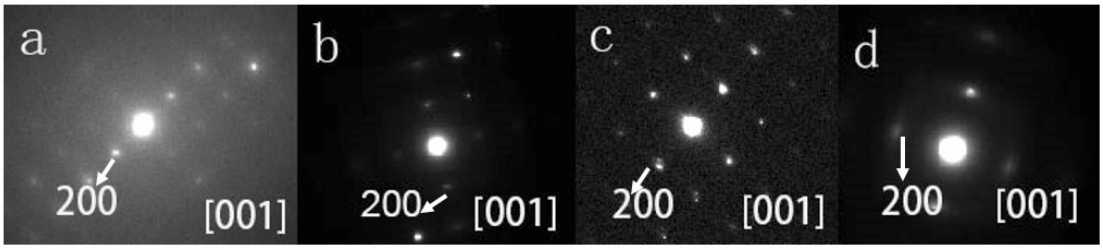


**Figure S2.** SEM images of the PBA crystals before (a) and after etching for b) 1, (c) 5, and (d) 10 minutes.

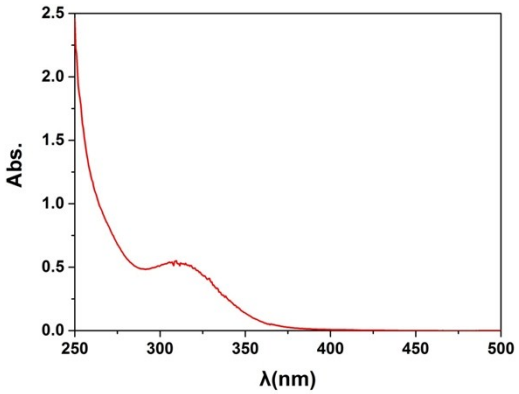


**Figure S3.** UV–vis spectra of supernatant of the reactant after etching of PBA with HCl for 10 minutes.

**Table S1**. Element distribution based on Element Analysis and ICP-MS

| Sample | Stoichiometry | Na(wt%) | Fe(wt%) | C(wt%) | N(wt%) |
|---|---|---|---|---|---|
| NaFe | $Na_{0.50}Fe[Fe(CN)_6]_{0.71}$ | 4.875 | 40.411 | 21.613 | 26.795 |
| NaFe-1 | $Na_{0.41}Fe[Fe(CN)_6]_{0.58}$ | 4.575 | 40.101 | 20.072 | 25.097 |
| NaFe-5 | $Na_{0.48}Fe[Fe(CN)_6]_{0.66}$ | 4.775 | 40.121 | 20.433 | 25.625 |
| NaFe-10 | $Na_{0.50}Fe[Fe(CN)_6]_{0.70}$ | 4.725 | 40.221 | 20.741 | 25.532 |

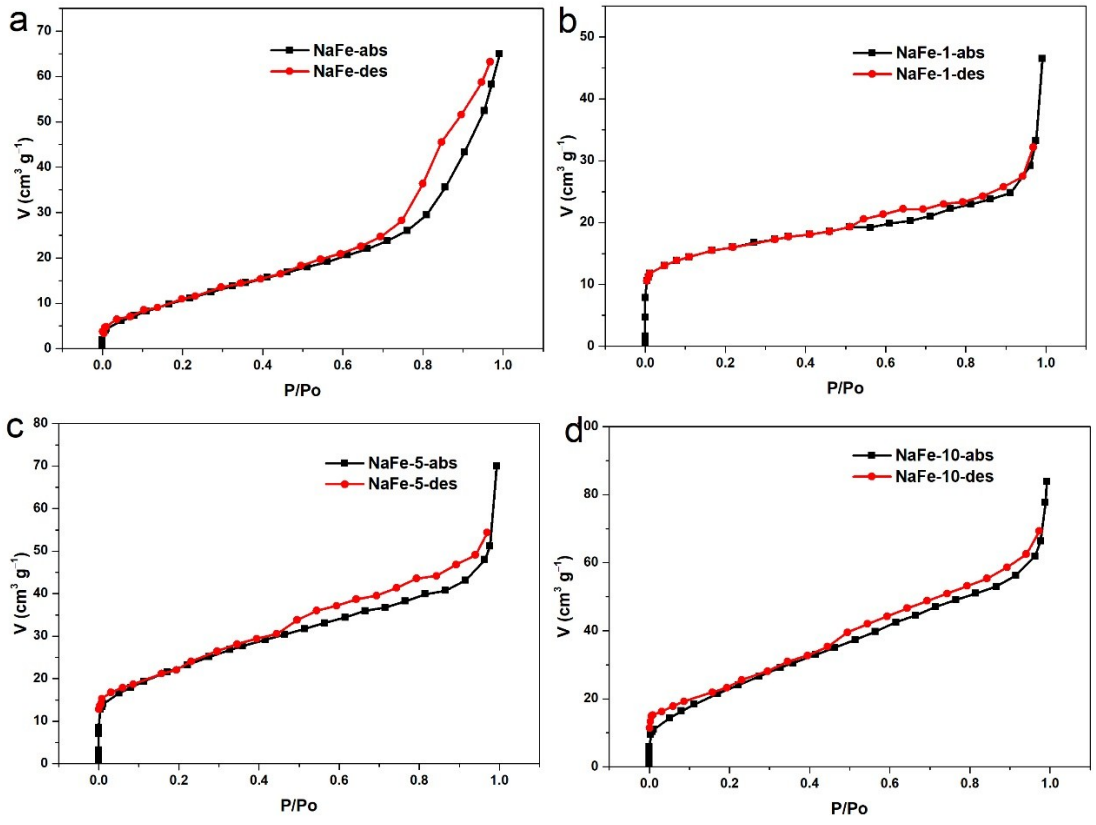

**Figure S4.** Brunauer-Emmett-Teller (BET) surface area of (a-d) PBA samples.

**Table S2.** BET surface area of PBA samples

| Sample | Surface area ($m^2$ $g^{-1}$) |
|---|---|
| **NaFe** | 43.5 |
| **NaFe–1** | 55.2 |
| **NaFe–5** | 81.7 |
| **NaFe–10** | 92.4 |

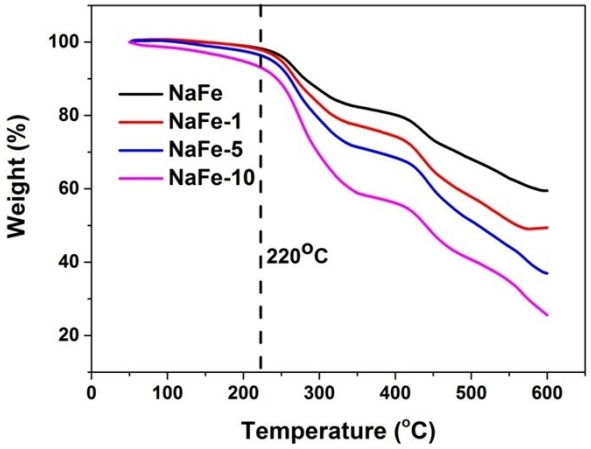


**Figure S5.** TGA curves of PBA in the temperature range from 50 to 600 °C under protection of $N_2$ with a heating rate of 10 °C $min^{-1}$. With the evolution of etching time, the water content in the sample increase step by step from NaFe–1 to NaFe–10, showing water content 1%, 1%, 3.9%, 6.8%, respectively. This might attribute to the broke morphology as a result of HCl, which release pathway for water to diffuse into samples.

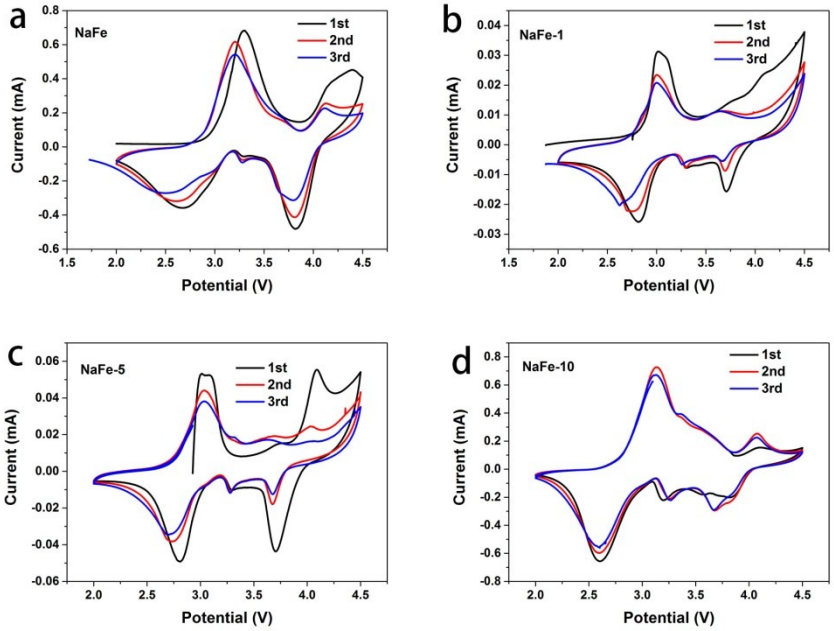


**Figure S6.** Cycling voltammogram of (a-d) PBA at 1 mV $s^{-1}$ between the potential window from 2.0 to 4.5 V.

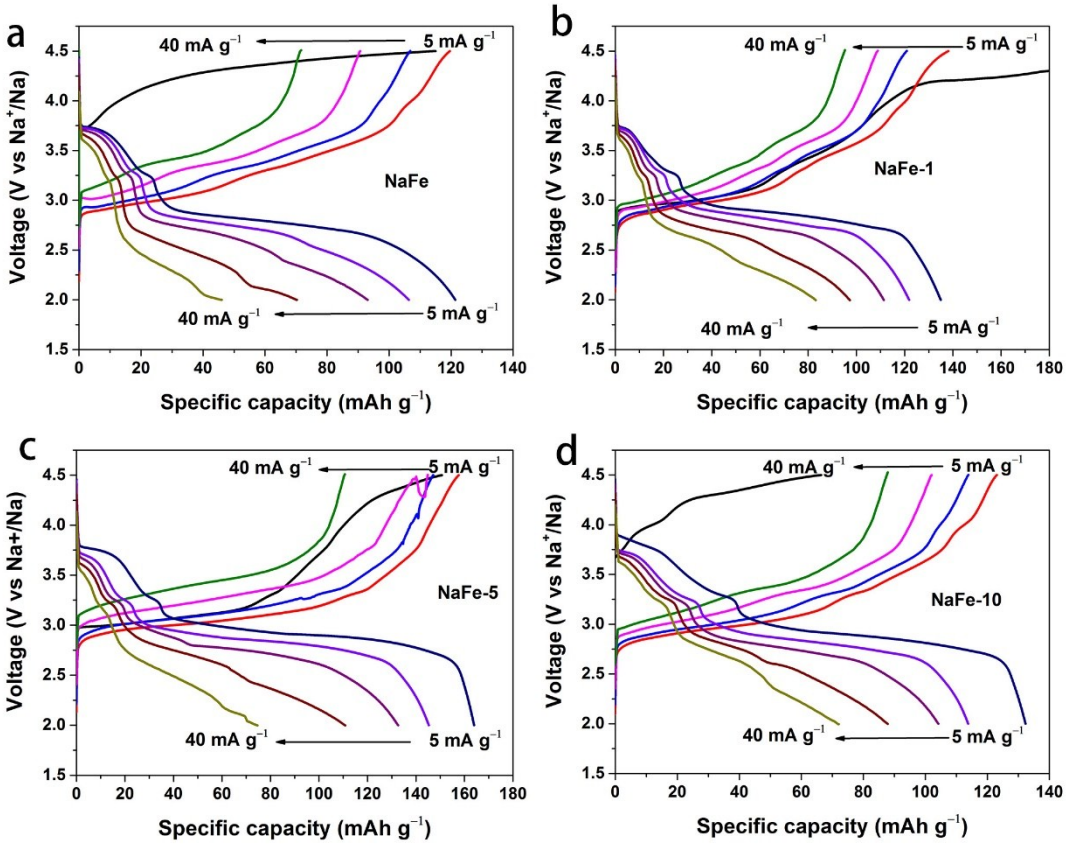


**Figure S7.** Galvanostatic discharge/charge voltage profiles of (a-d) PBA under different

current densities.

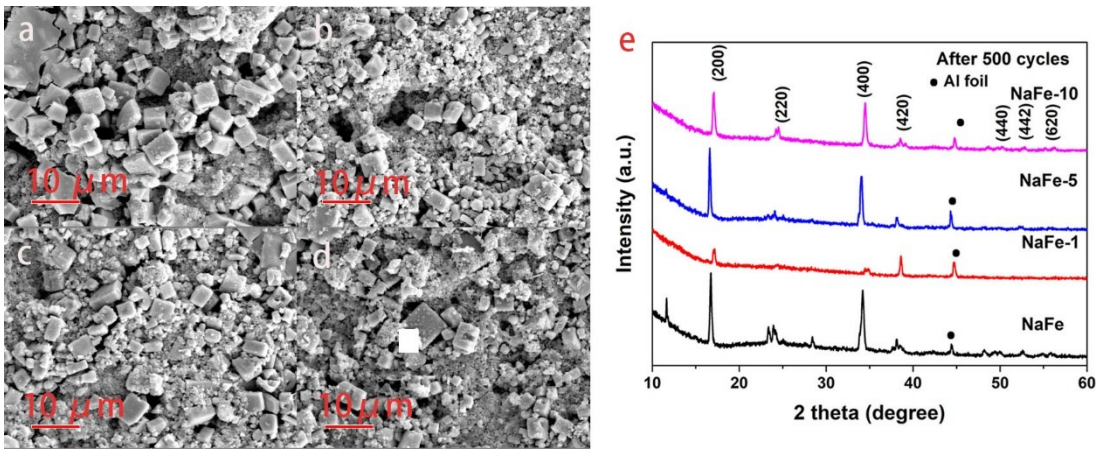


**Figure S8.** (a-d) SEM images and (e) XRD patterns of PBA after 500 cycles.

**Table S3.** Comparison of resistance of charge transfer resistance ($R_{ct}$) and resistance of solution ($R_s$) before cycle and after 500 cycles

| Sample | $R_s$(before cycle) | $R_{ct}$(before cycle) | $R_s$(after cycle) | $R_{ct}$(after cycle) |
|---|---|---|---|---|
| **NaFe** | 7.1 | 1646 | 24.3 | 3940 |
| **NaFe–1** | 4.7 | 1200 | 6.9 | 1859 |
| **NaFe–5** | 7.5 | 474.6 | 12.4 | 2522 |
| **NaFe–10** | 7.3 | 794.5 | 25.8 | 1107 |

**Table S4.** Comparison of diffusion coefficients before and after 500 cycles

| Sample | $D_{Na^+}$(before cycle) ($cm^2\ s^{-1}$) | $D_{Na^+}$(after cycles) ($cm^2\ s^{-1}$) |
|---|---|---|
| **NaFe** | $5.2*10^{-11}$ | $4.3*10^{-10}$ |
| **NaFe–1** | $1.7*10^{-10}$ | $3.5*10^{-9}$ |
| **NaFe–5** | $2.3*10^{-10}$ | $5.1*10^{-10}$ |
| **NaFe–10** | $2.8*10^{-10}$ | $7.0*10^{-9}$ |

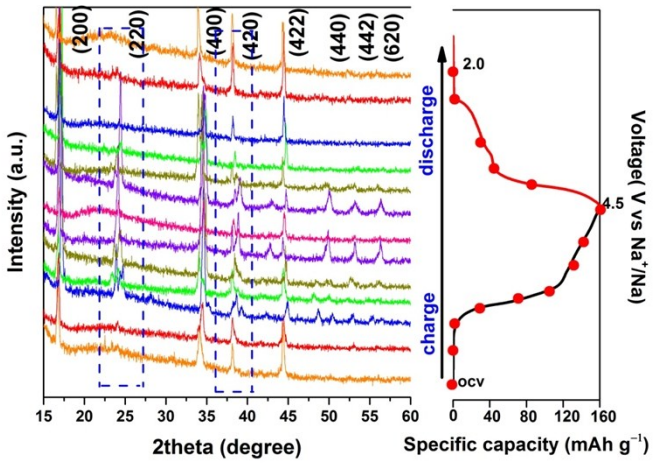


**Figure S9.** *Ex situ* XRD patterns of pristine PBA at different charge and discharge state.