Effect of synthesis pH and EDTA on iron hexacyanoferrate for sodium-ion batteries

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Electronic Supplementary Information

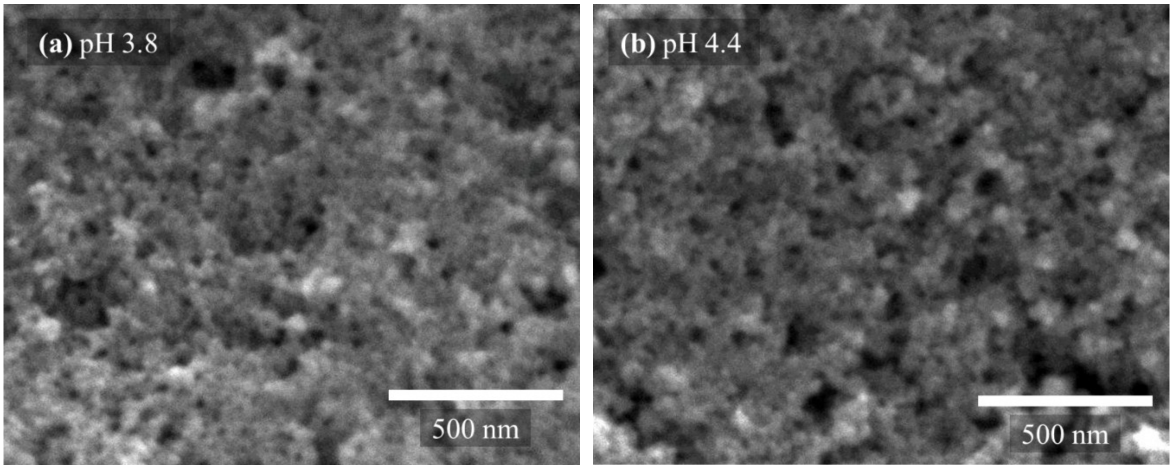

Figure S1. SEM micrographs of FeHCF synthesized without EDTA at pH 3.8 (a) and pH 4.4 (b).

Table S1. Fitting parameters for Mössbauer spectra. is the isomer shift relative to -Fe in mm/s, is the quadrupole splitting in mm/s, and is the full line width at half max in mm/s. The quadrupole splitting displayed for high-spin Fe(III) and Fe(II) is the weighted average of the three doublets.

	Low-Spin Fe(II)				**High-Spin Fe(III)**				**High-Spin Fe(II)**				**Ratio**
	δ	ΔE_Q	Γ	Area %	δ	$\langle \Delta E_Q \rangle$	Γ (fixed)	Area %	δ	$\langle \Delta E_Q \rangle$	Γ (fixed)	Area %	LS : HS
PB(3.8)	-0.19	0.14	0.34	45	0.41	0.14	0.34	55	-	-	-	0	0.82 : 1
PB(4.4)	-0.18	0.00	0.37	49	0.42	0.11	0.34	43	1.06	0.18	0.34	9	0.96 : 1

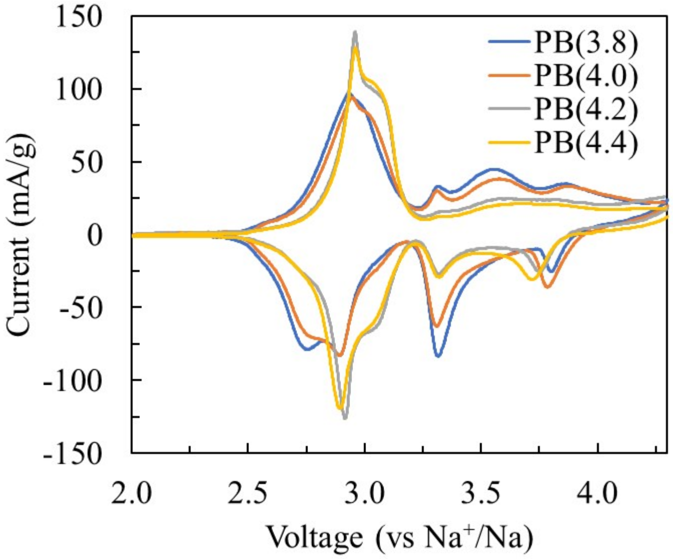

Figure S2. Cyclic voltammetry of first cycle after initial galvanostatic oxidation at 100 mA/g to 4.3 V.

After initial synthesis, PB(3.8) particles were washed in pH 4.4 buffer solution and PB(4.4) particles washed in pH 3.8 buffer solution for 24 hours to test whether surface chemistry change due to pH had any effect on cyclability. The cyclic performance of the FeHCF particles did not change after washing in different pH solutions, and capacity retention remained nearly the same at 86 and 94% for PB(3.8) and PB(4.4), respectively (Figure S4).

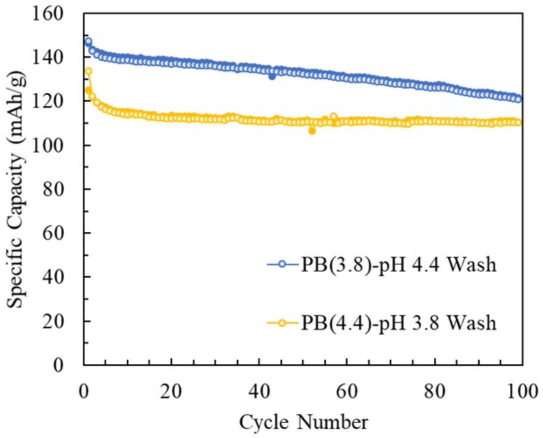

Figure S3. Galvanostatic cycling at 100 mA/g for PB(3.8) washed for 24 hours in pH 4.4 solution and PB(4.4) washed for 24 hours in pH 3.8 solution.

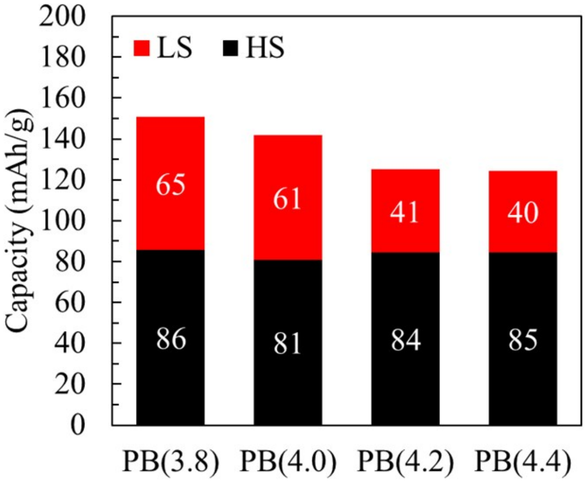

Figure S4. High-spin and low-spin Fe reduction capacity contributions for first discharge cycle at 100 mA/g. Low-spin capacity contribution approximated as discharge capacity associated with the high-voltage plateau.

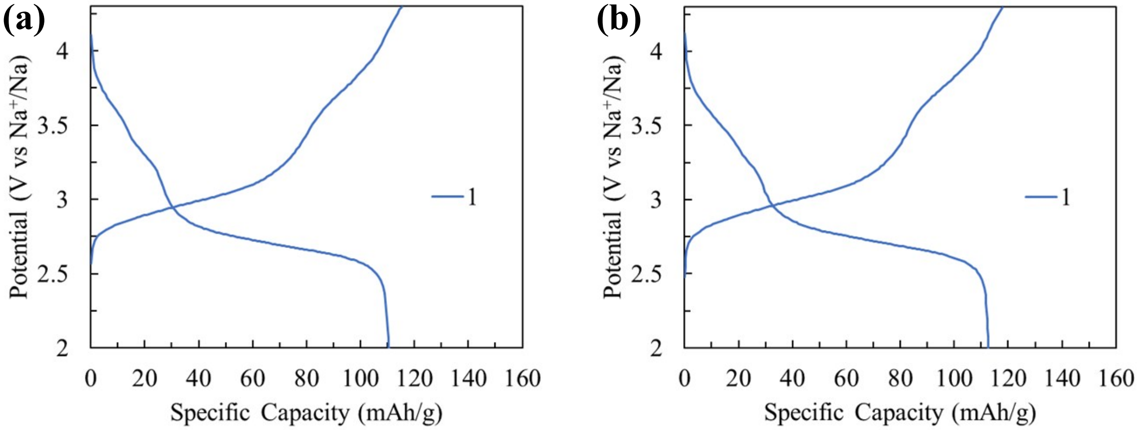

Figure S5. Galvanostatic profile at 100 mA/g of FeHCF synthesized without EDTA at pH 3.8 (a) and pH 4.4 (b).

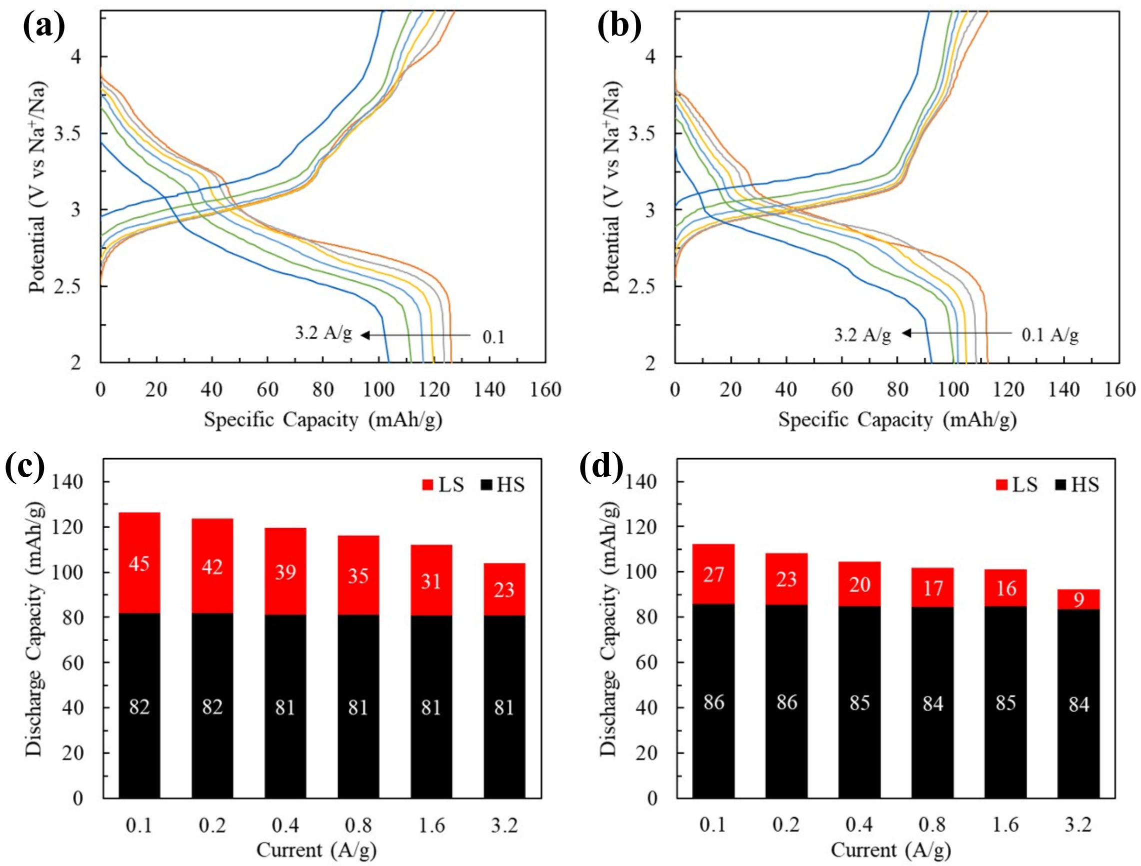

Figure S6. Rate performance of PB(4.0) (a) and PB(4.2) (b), and their respective estimated capacity contributions between low-spin and high-spin Fe (c&d).

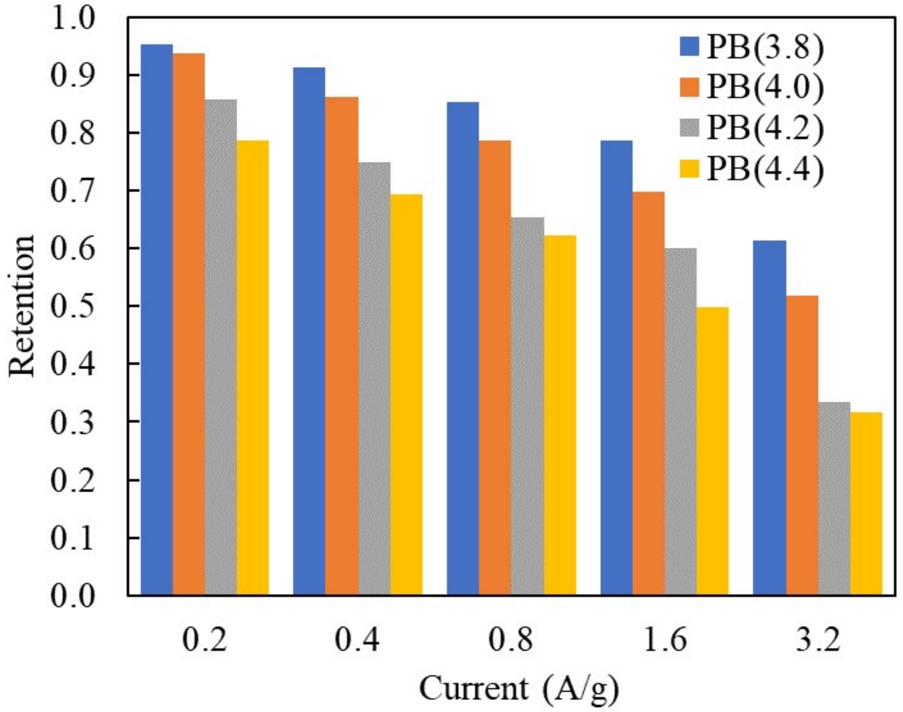

Figure S7. Approximate capacity retention of low-spin Fe reduction at increasing discharge rate compared to 0.1 A/g.

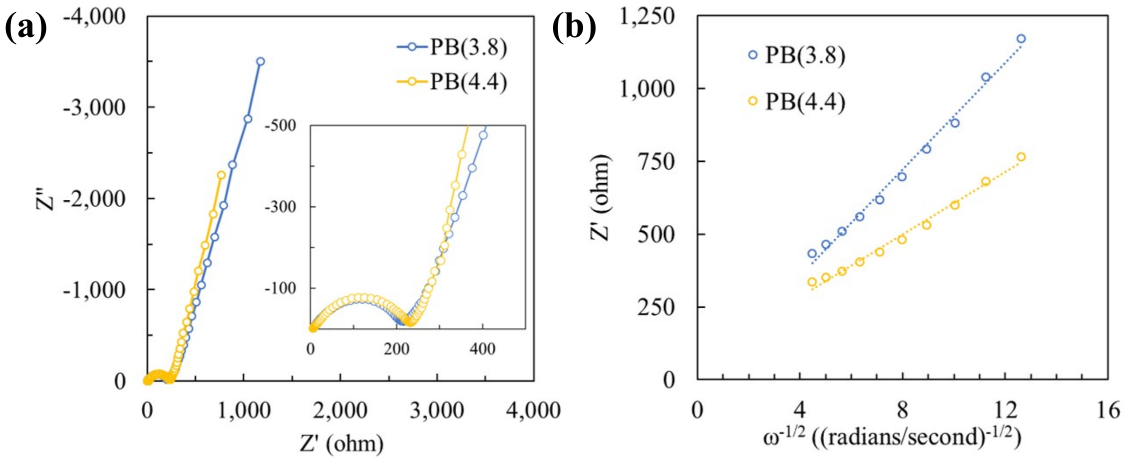

Figure S8. EIS spectra of PB(3.8) and PB(4.4) in the charged state after galvanostatic cycling (a). Plot of real impedance vs inverse square root of angular frequency (b).