Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis, Characterisation and Enhanced Electrochemical Performance of Nanostructured Na_2FePO_4F for Sodium Batteries

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Supporting information

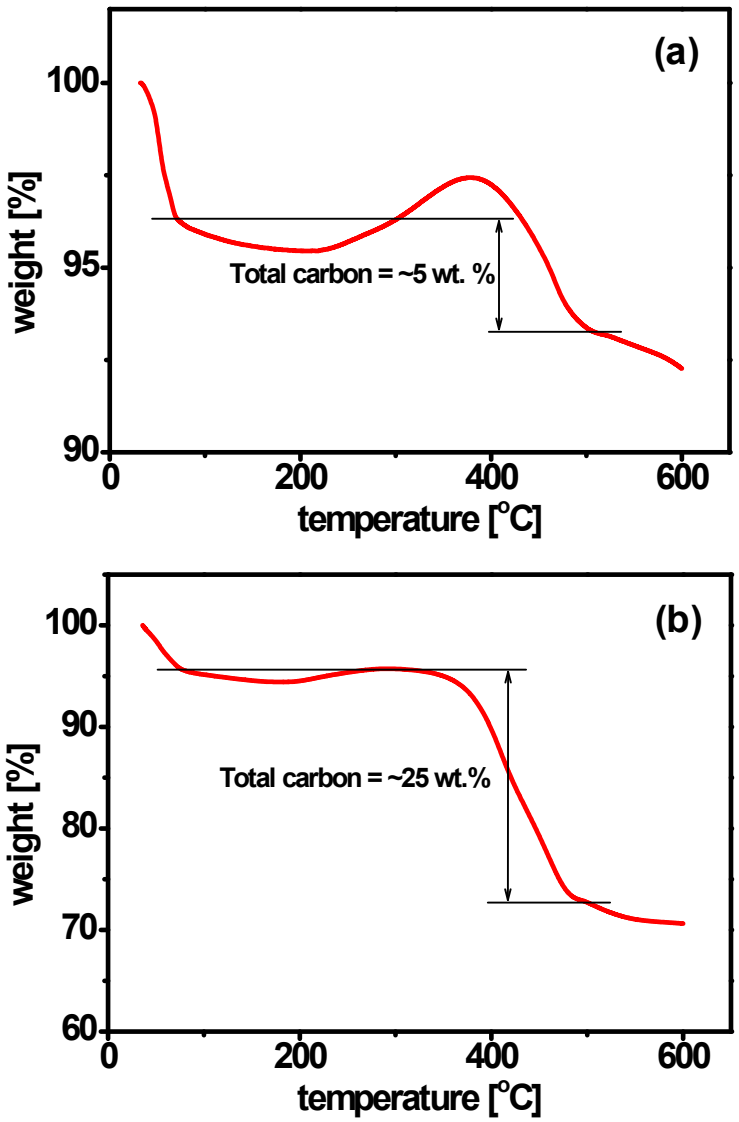

Fig. S1. TGA curves of (a) pristine; and (b) HEBM Na_2FePO_4F samples obtained at a heating rate of 5°C min^{-1} from room temperature to 600°C.

From the TGA curves (**Fig. S1**), the decrease in weight from room temperature to around 100°C is attributed to the release of water of crystallization.[1, 2] Therefore, the carbon content measurement is taken from ~100°C onwards.

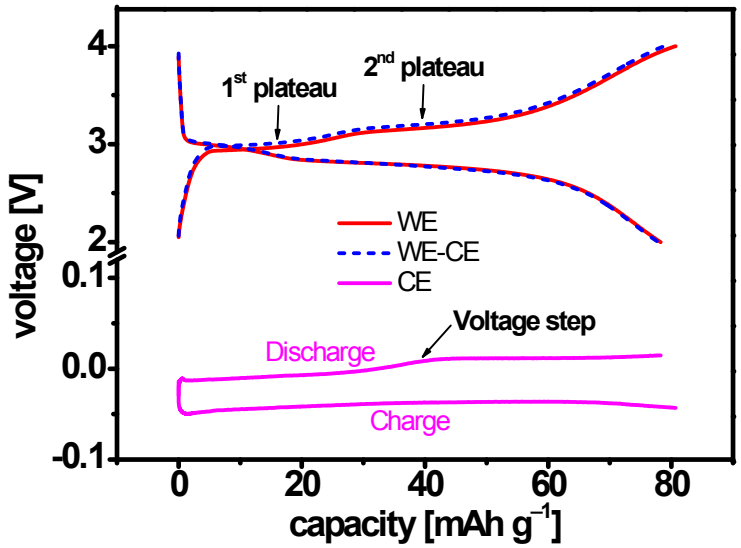

Fig. S2. Three-electrode galvanostatic cycling at 1 C of the Na_2FePO_4F WE electrode against the Na CE and RE.

Galvanostatic cycling was conducted on a three-electrode cell at 1 C with the HEBM sample as the working electrode (WE) and metallic sodium as the reference electrode and counter electrode (CE). The resulting voltage profile is shown in **Fig. S2**. As can be seen, the two-voltage plateaus observed during charging and discharging arises from the electrochemical activity of the WE itself and not from the formation of a passivation film on the CE. [3] Although the CE displays a voltage step during discharge due to the formation of a passivation film, the two-voltage plateau is still clearly visible on the WE profile, which further clarifies that this two-voltage profile belongs to the WE.

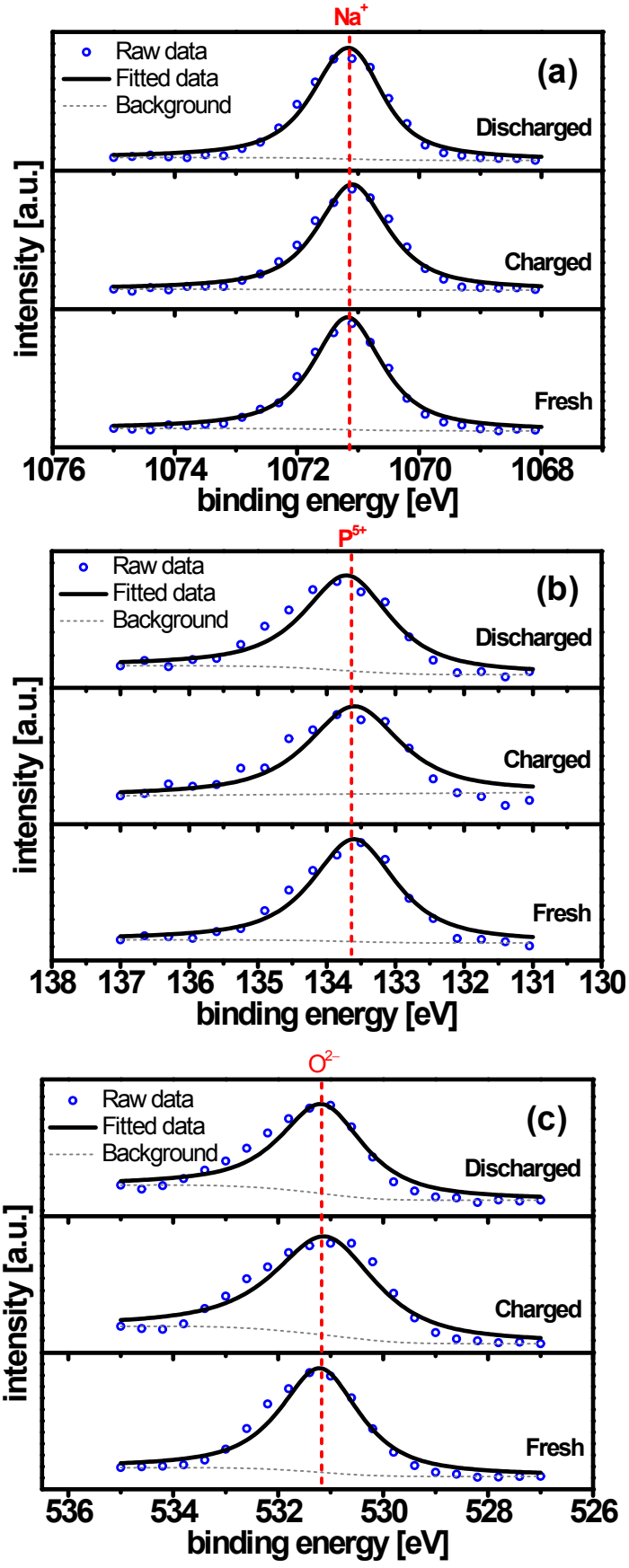

Fig. S3. *Ex-situ* XPS spectra of (a) Na^{+}; (b) P^{5+}; and (c) O^{2-} obtained on a fresh, charged and discharged electrode.

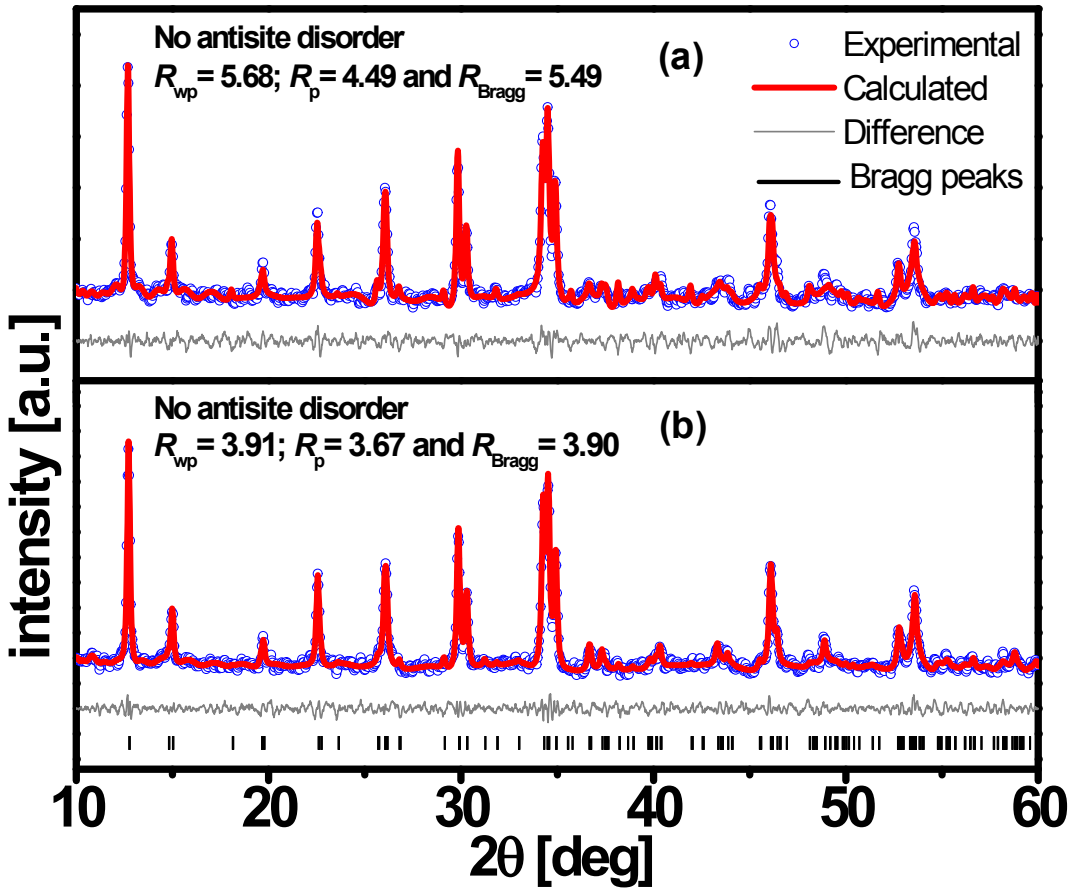

Fig. S4. Rietveld refinement profile of the (a) pristine; and (b) HEBM sample with no antisite disorder.

Table S1. Site occupancies and percentage of iron in sodium sites of the pristine sample.

R_{wp} = 2.84; R_p = 2.22 and R_{Bragg} = 2.04; space group: *Pbcn*

Site	Ions	*x*	*y*	*z*	Occ (th)	Occ (calc)
Na1	Na^+	0.22029	0.24281	0.31448	1	0.9925
	Fe^{2+}				0	0.0071
Na2	Na^+	0.25313	0.1303	0.07528	1	0.9935
	Fe^{2+}				0	0.0070
Fe1	Fe^{2+}	0.24112	0.01103	0.32912	1	0.9857
	Na^+				0	0.0075
	Na^+				0	0.0069
P1	P^{5+}	0.22406	0.38236	0.08666	1	1
F1	F^-	0	0.13296	0.25	1	1
F2	F^-	0.5	0.12725	0.25	1	1
O1	O^{2-}	0.29233	0.36647	-0.03597	1	1
O2	O^{2-}	0.35626	0.30436	0.14498	1	1
O3	O^{2-}	-0.14665	0.37767	0.09832	1	1
O4	O^{2-}	0.33977	0.47016	0.13837	1	1
Total % of Fe occupying Na sites = 1.41%						

Table S2. Site occupancies and percentage of iron in sodium sites of the HEBM sample.

R_{wp} = 2.19; R_p = 1.73 and R_{Bragg} = 2.34; SG: Pbcn

Site	Ions	*x*	*y*	*z*	Occ (th)	Occ (calc)
Na1	Na^+	0.25804	0.24388	0.31509	1	0.9988
	Fe^{2+}				0	0.0021
Na2	Na^+	0.22264	0.1473	0.09175	1	0.9985
	Fe^{2+}				0	0.0027
Fe1	Fe^{2+}	0.2646	-0.00433	0.3422	1	0.9981
	Na^+				0	0.0011
	Na^+				0	0.0010
P1	P^{5+}	0.26813	0.38391	0.05545	1	1

F1	F^-	0	0.12212	0.25	1	1
F2	F^-	0.5	0.07716	0.25	1	1
O1	O^{2-}	0.3119	0.38407	-0.07688	1	1
O2	O^{2-}	0.33593	0.29738	0.13674	1	1
O3	O^{2-}	-0.04772	0.37534	0.12525	1	1
O4	O^{2-}	0.28851	0.47739	0.1622	1	1
Total % of Fe occupying Na sites = 0.48%						

From the tables above, the pristine Na_2FePO_4F sample exhibits the most antisite disorder, with a total concentration of 1.41% of its Fe^{2+} simultaneously occupying both the Na sites. The HEBM sample shows the least antisite disorder, with just a total of 0.48% Fe^{2+} simultaneously occupying both the Na sites.

References

1. J. Yu, J. Hu and J. Li, *Applied Surface Science*, 2012, **263**, 277-283.
2. P. P. Prosini, P. Gislon, C. Cento, M. Carewska and A. Masci, *Materials Research Bulletin*, 2013, **48**, 3438-3448.
3. A. Rudola, D. Aurbach and P. Balaya, *Electrochemistry Communications*, 2014, **46**, 56-59.