SUPPORTING INFORMATION

Understanding Dehydration of Prussian White: from Material to Aqueous Processed Composite Electrodes for Sodium-Ion Battery Application

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Content:

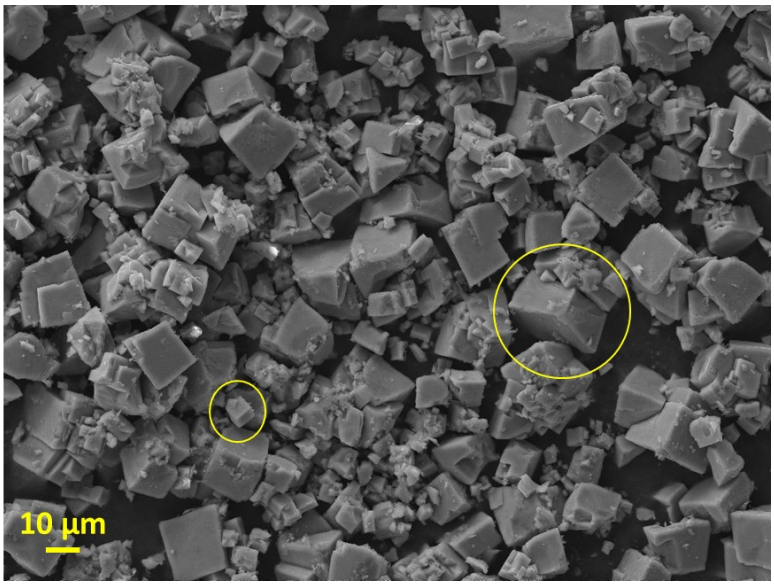

Figure S1. SEM image of pristine PW material in its pristine monoclinic phase.

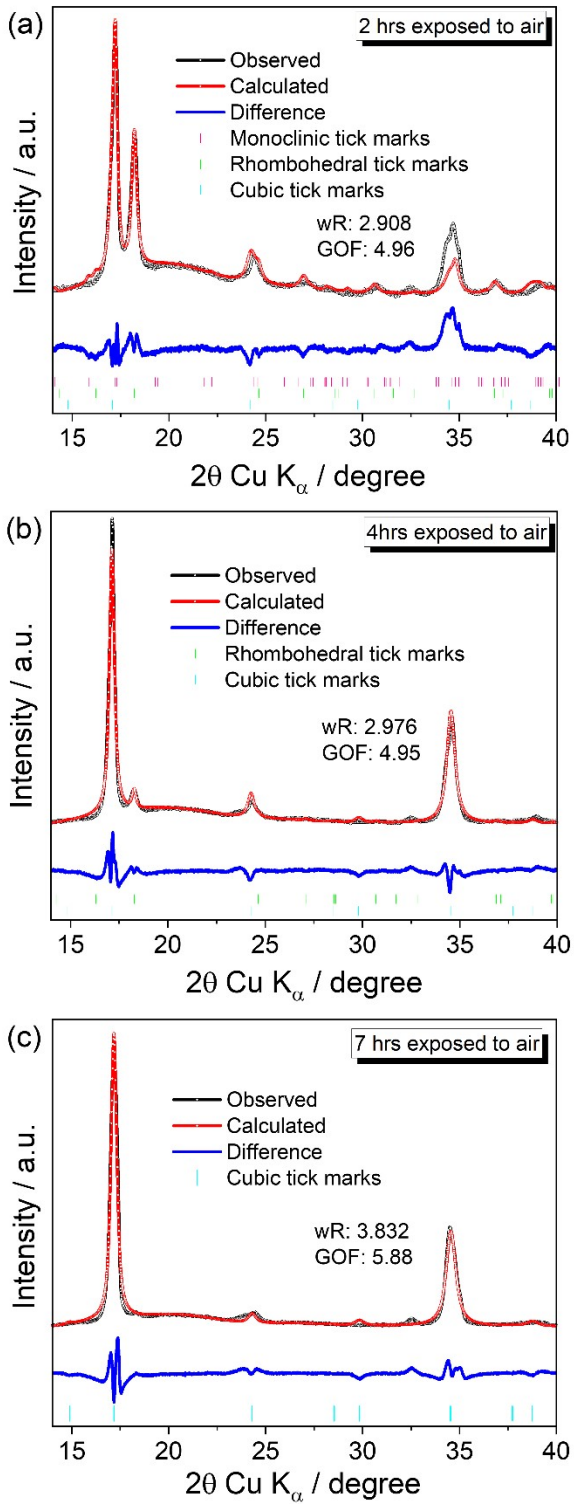

Figure S2. Fitted XRD patterns of dehydrated PW powders (15 hours) exposed to air/moisture for 2, 5 and 7 hours.

Table S1. Refined structural parameters for fitted data reported in Fig. S1 (dehydrated PW powders exposed in air/moisture for 2, 4, and 7 hours).

Exposed samples	**Monoclinic ($P2_1/n$)**					**Cubic (Fm-3m)**		**Rhombohedral (R-3)**		
	a (Å)	b (Å)	c (Å)	β (°)	vol (Å3)	a (Å)	vol ($Å^3$)	a (Å)	c (Å)	vol ($Å^3$)
Pristine powder	10.4543(9)	7.4441(9)	7.2865(8)	92.712(14)	566.431(28)					
Powder dried 15 hrs	10.3277(8)	7.0459(6)	7.5946(7)	91.725(17)	552.391(23)			6.5476(4)	19.007(4)	705.67(3)
Powder 15 hr exposed 2 hr	10.3219(19)	6.709(10)	8.046(17)	90.71(10)	557.2(7)	10.4155(18)	1129.9(6)	6.624(5)	18.644(23)	708.47(31)
Powder 15 hr exposed 4 hr						10.4207(15)	1131.6(4)	6.609(13)	18.77(6)	710.1(8)
Powder 15 hr exposed 7 hr						10.4329(4)	1135.59(12)			

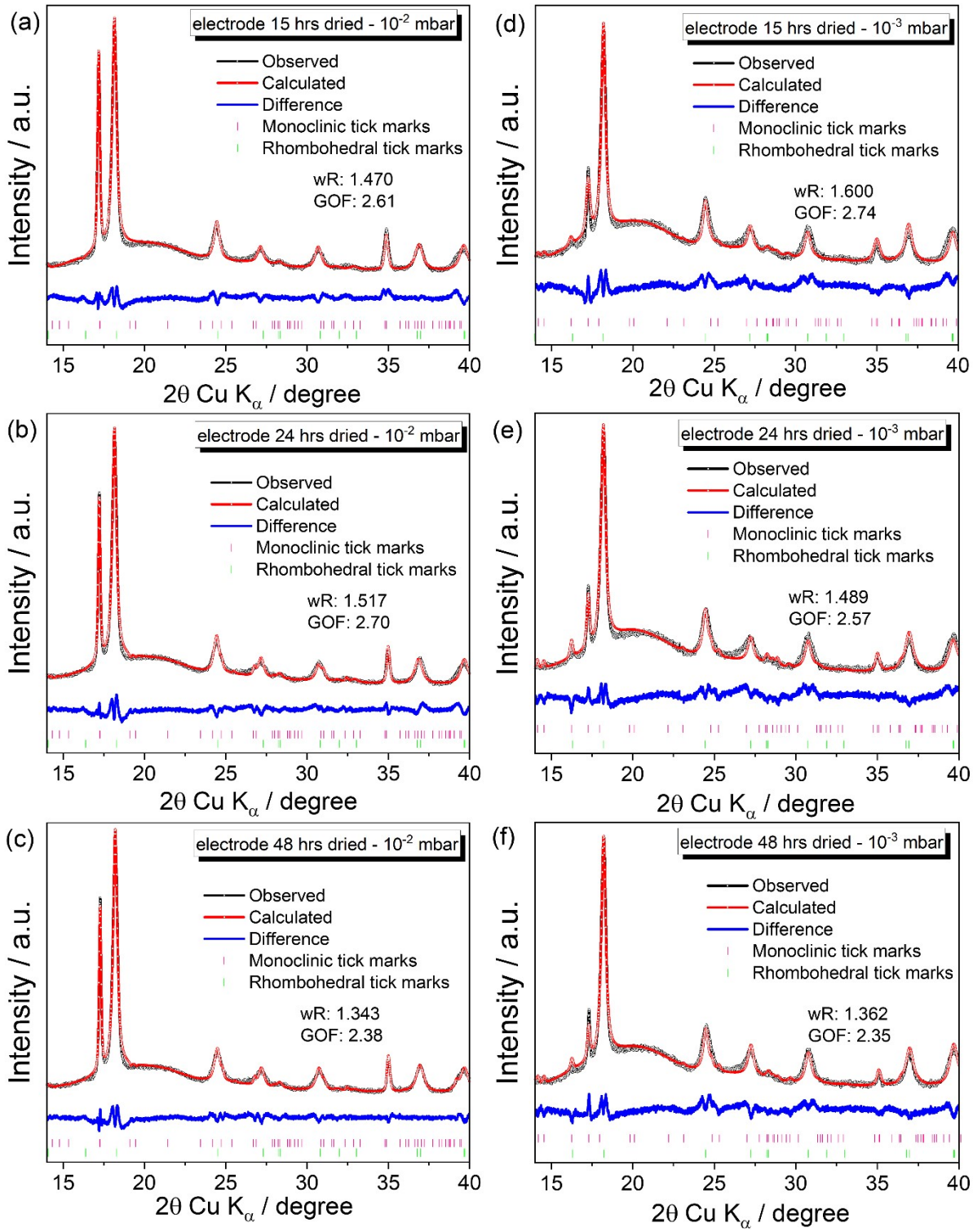

Figure S3. Fitted XRD patterns of dehydrated PW electrodes dried at 170 ˚C for 15, 24, and 48 hours under dynamic vacuum conditions at 10^{-2} mbar (a-c) and at 10^{-3} mbar (d-f).

Table S2. Refined structural parameters for fitted data reported in Fig. S2.

10^{-2} mbar	Monoclinic ($P2_1/n$)					Rhombohedral (R-3)		
	a (Å)	b (Å)	c (Å)	β (°)	vol ($Å^3$)	a (Å)	c (Å)	vol ($Å^3$)
Electrode 15 hrs	10.2770(24)	7.040(5)	7.506(5)	91.54(3)	542.88(33)	6.5563(9)	18.882(7)	702.92(5)
Electrode 24 hrs	10.2310(21)	6.952(3)	7.554(3)	91.70(5)	537.16(28)	6.5378(9)	18.877(3)	698.80(7)
Electrode 48 hrs	10.2552(16)	6.9507(18)	7.5751(18)	91.817(31)	539.71(5)	6.5520(9)	18.898(3)	702.61(6)
10^{-3} mbar	Monoclinic ($P2_1/n$)					Rhombohedral (R-3)		
Electrode 15 hrs	10.238(4)	6.437(8)	7.666(12)	91.53(8)	505.0(9)	6.5341(27)	18.912(5)	699.3(4)
Electrode 24 hrs	10.2426(26)	6.417(3)	7.694(6)	91.65(4)	505.5(4)	6.5374(25)	18.944(5)	701.2(4)
Electrode 48 hrs	10.2181(27)	6.411(4)	7.678(6)	91.50(5)	502.8(5)	6.5342(24)	18.912(4)	699.3(4)

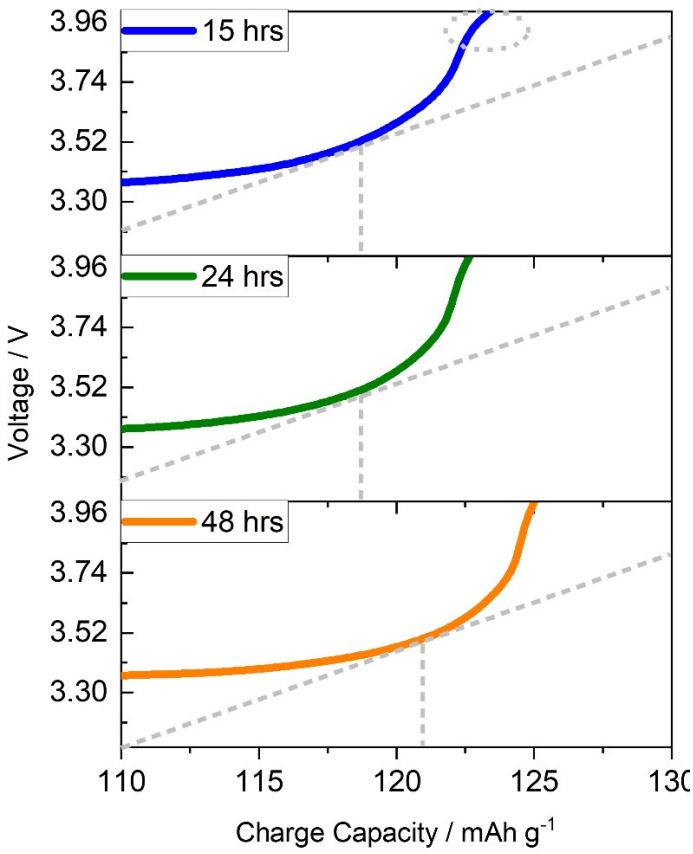

Fig. S4 Selected zoomed high voltage region of Fig. 7 for electrodes dried at 170 °C for 15, 24 and 48 hours under dynamic vacuum at 10^{-2} mbar, showing features attributable to the presence of residual water (above 3.8 V) and its progressive decrease upon drying.

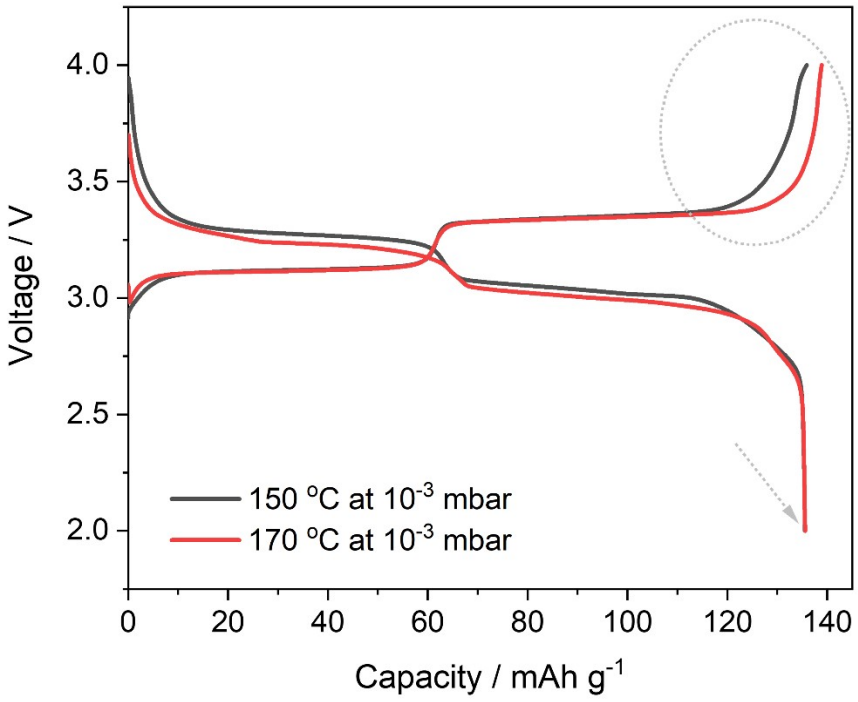

Figure S5. First charge/discharge voltage profiles of Na half cells containing PW electrodes dried at 150°C and 170 °C under a dynamic vacuum of 10^{-3} mbar. Test conducted at 25 °C using 1M $NaPF_6$ in diglyme electrolyte within the 2.0 - 4.0 V range. (C/10, 1C=140 mA g^{-1}).

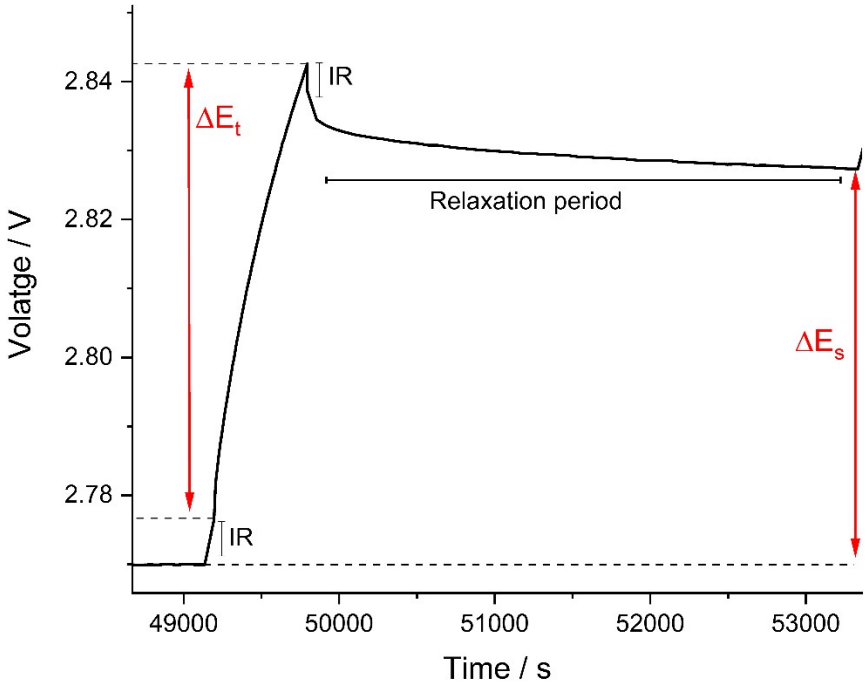

Figure S6. Example plot of a single step for a GITT test.

The Na^+ diffusion coefficient was calculated by using the following simplified Eq. (1)[1,2]:

$$D = \frac{4}{\pi\tau}\cdot\left(\frac{m V_m}{MS}\right)^2 \cdot \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \qquad (1)$$

Where *m*, V*m*, and *M* represent the active mass, the molar volume, and the molar mass of the PW material, respectively. τ denotes the duration of a current pulse, and S is the electrode surface area. ΔE_t represents the total change of cell voltage during a constant current pule of a single-step GITT (neglecting the IR-drop), and ΔEs is the voltage variation during a current pulse in two adjacent GITT process, as illustrated in Figure S5.

Table S3. Parameters used to calculate diffusion coefficient of a representative PW electrode.

Electrode active mass	23.898 mg
Electrode area	1.72 cm^2
Electrode thickness	85 μm
PW molecular weight ($Na_{1.80(5)}$ Fe [Fe $(CN)_6$] ·1.84(3) H_2O)	343.429 g mol^{-1}

Molar volume was obtained by initially calculating the number of moles through Eq. (2). Following on, Eq. (3) was used to calculate the volume of the electrode. The resulting values were then incorporated into Eq. (4) to obtain the molar volume.

$$Moles = \frac{Active\ mass}{Molecular\ weight} \quad (2)$$

$$Volume = Electrode\ area \cdot Electrode\ thickness \quad (3)$$

$$Molar\ volume = \frac{Volume}{Moles} \quad (4)$$

References

1 W. Wang, Y. Gang, Z. Hu, Z. Yan, W. Li, Y. Li, Q.-F. Gu, Z. Wang, S.-L. Chou and H.-K. Liu, *Nat. Commun.*, 2020, **11**, 980.

2 W. Ren, Z. Zhu, M. Qin, S. Chen, X. Yao, Q. Li, X. Xu, Q. Wei, L. Mai and C. Zhao, *Adv. Funct. Mater.*, 2019, **29**, 1806405.