

## Supporting Information

### **Hierarchical structural designs of ion exchange membranes for flow batteries**

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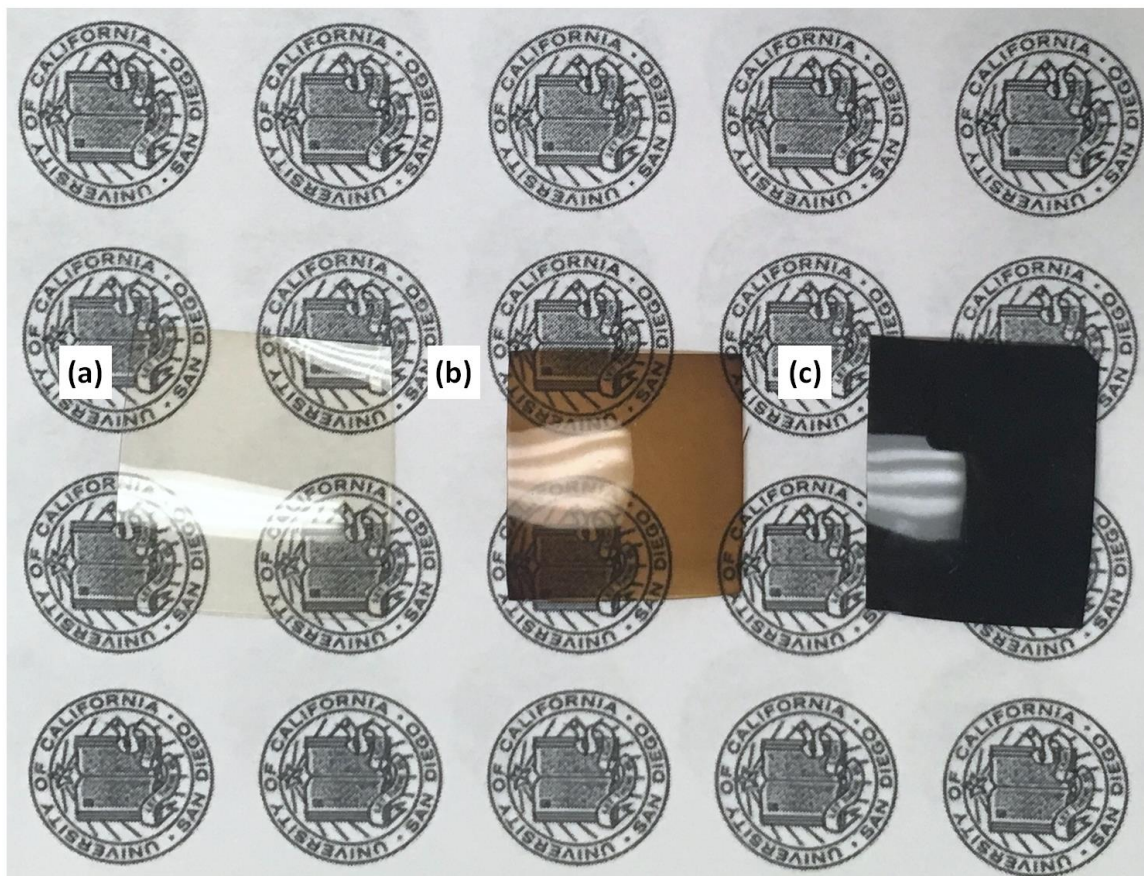


Figure S1. Photo of (a) Blank Nafion; (b) h-DNf/oxide; (c) c-DNf/oxide.

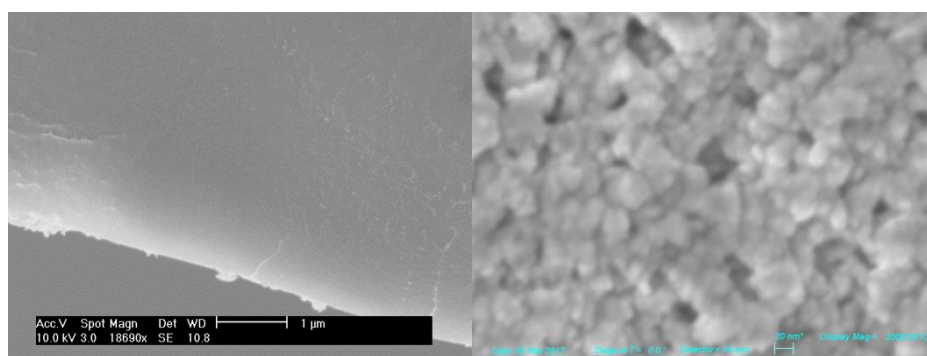


Figure S2. SEM images: (a) cross section of DNf; (b) ultra-high magnification surface of h-DNf/oxide.

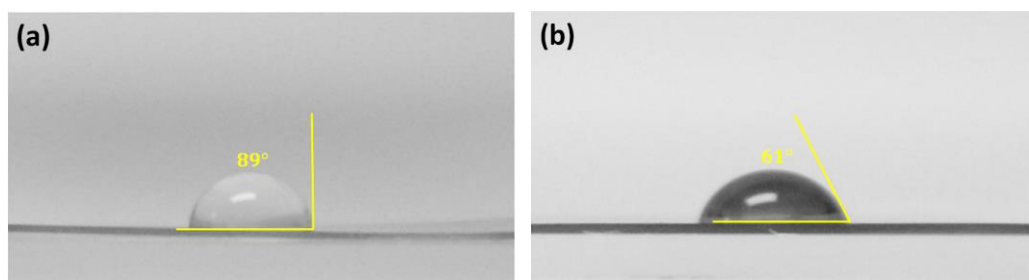


Figure S3. Contact angles of (a) Blank Nafion; (b) DNf.

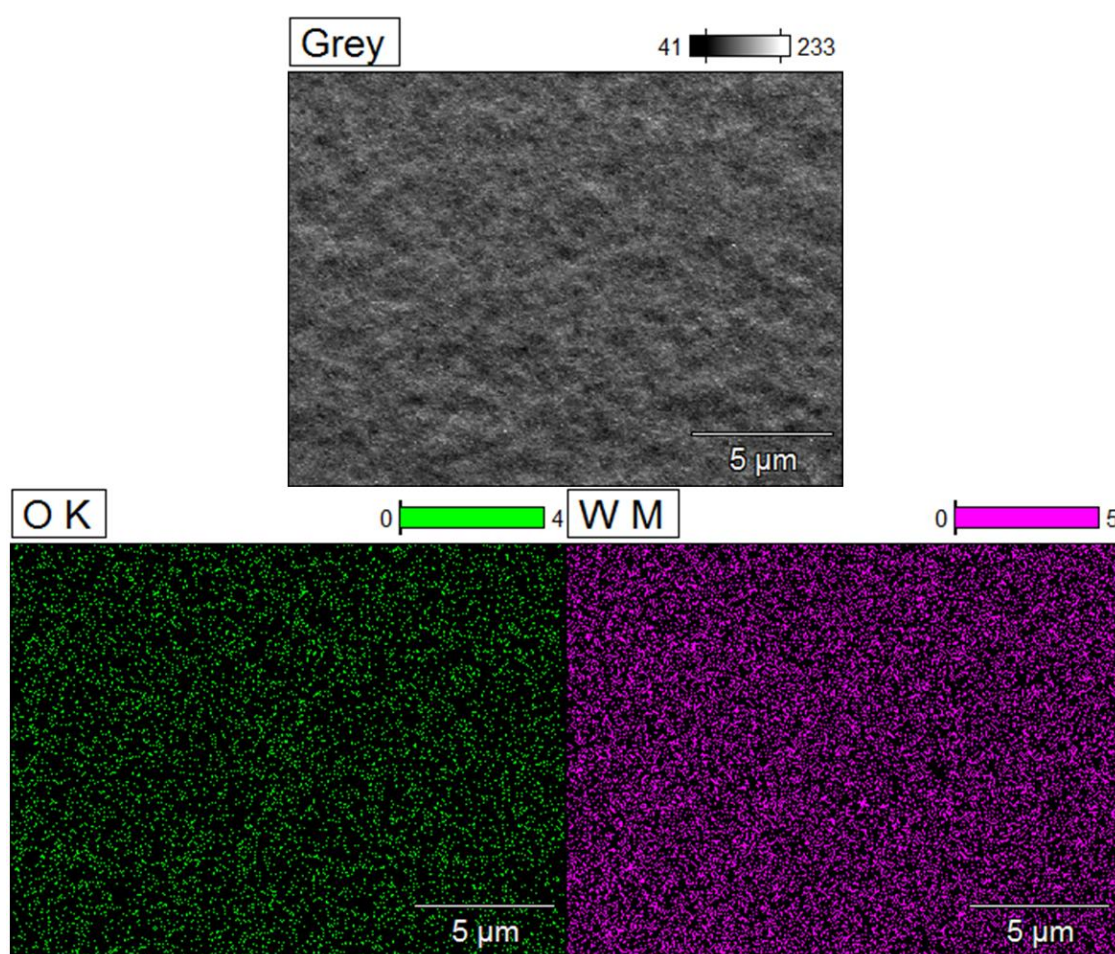


Figure S4. Surface EDX of h-DNf/oxide.



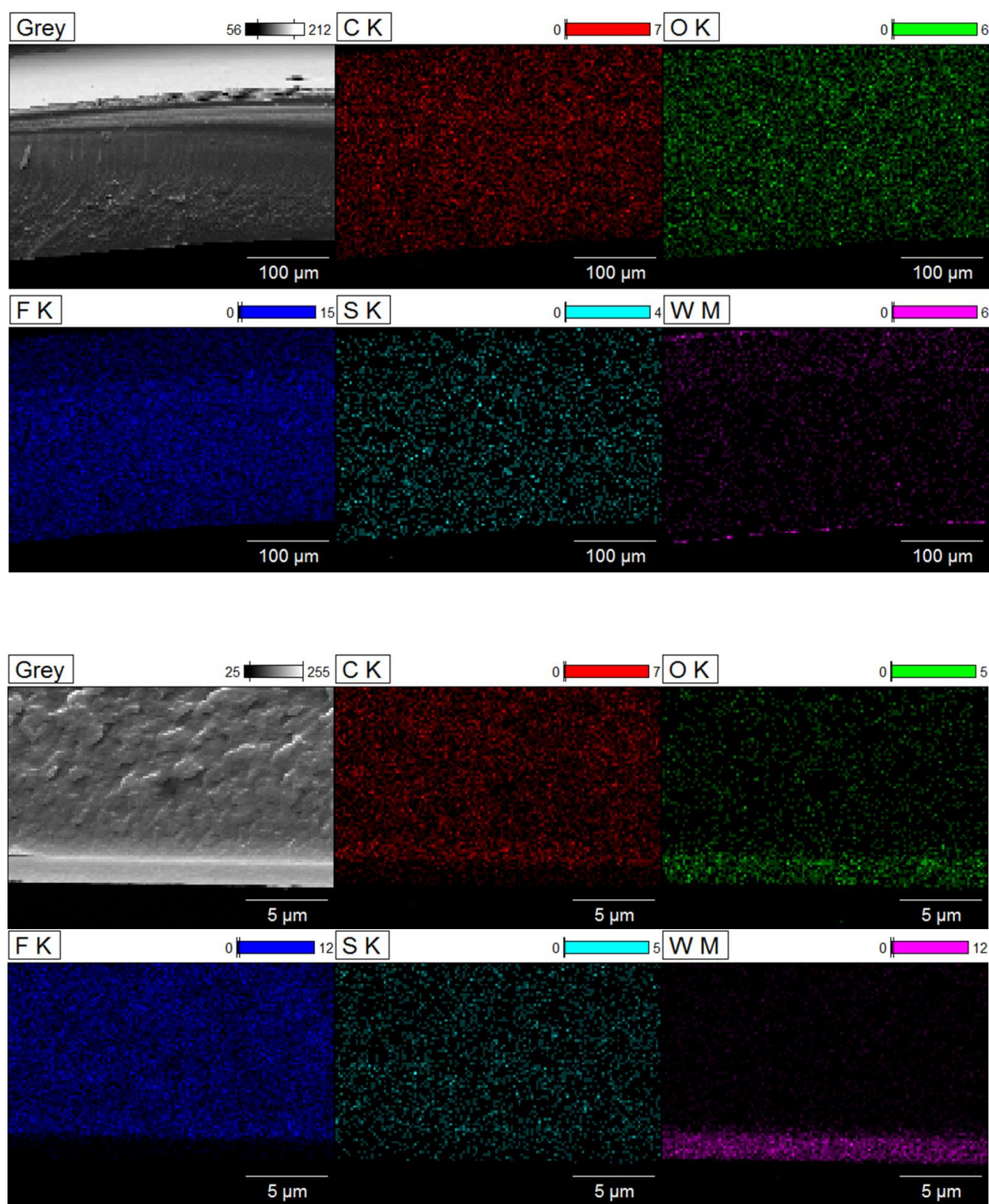


Figure S5. Surface EDX of h-DNf/oxide: (a) low magnification; (b) high magnification.

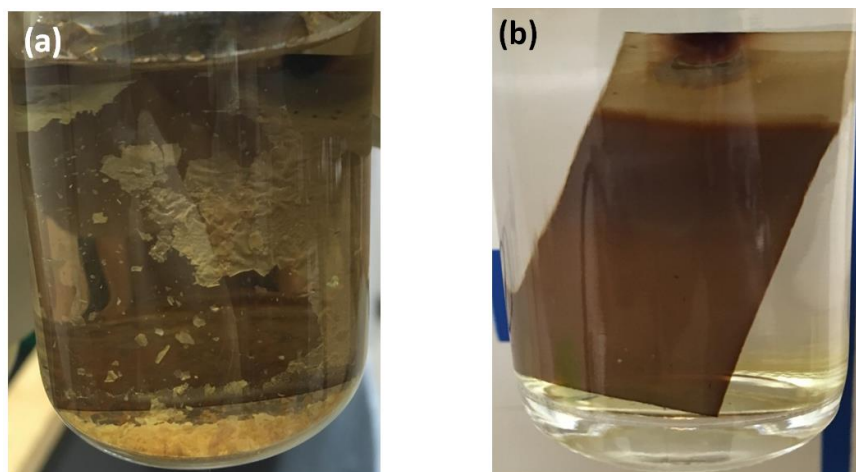


Figure S6. Stability of coating layer: (a) l-DNf/oxide soaked in DI water for 24 hours; (b) h-DNf/oxide soaked in DI water for 1 week.

Table S1. Mechanical properties of Nafion and h-DNf/oxide.

	Young's modulus	Yield stress	Yield strain	Ultimate stress	Ultimate strain
	[Mpa]	[Mpa]	[%)]	[Mpa]	[%]
Nafion-dry	142.5	7.67	8.5	25.9	223.3
Nafion-wet	35.5	4.95	22.0	20.4	233.4
h-DNf/oxide-wet	148.7	9.29	9.1	17.0	47.3

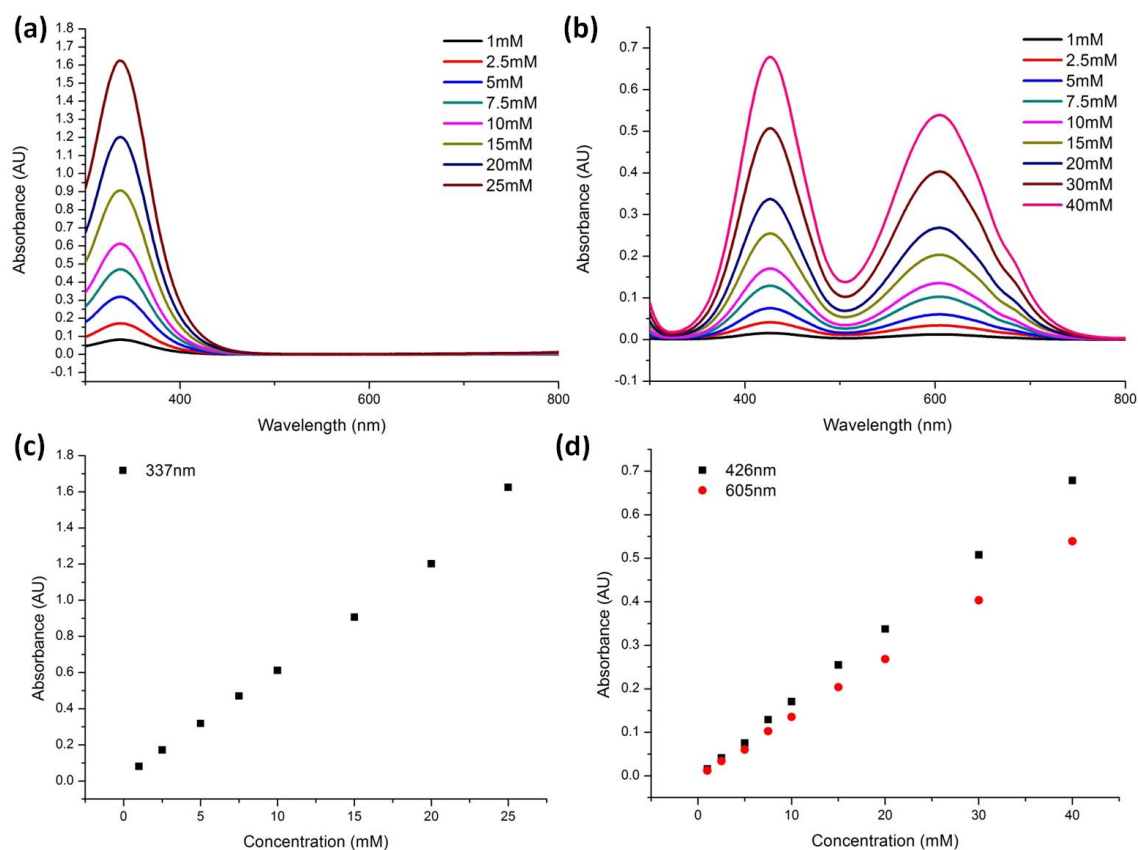


Figure S7. UV-vis on standard samples (a) UV-vis spectrums on  $\text{Fe}^{2+}$  standard samples; (a) UV-vis spectrums on  $\text{Cr}^{3+}$  standard samples; (c) concentration-absorbance standard curve of  $\text{Fe}^{2+}$ ; (d) concentration-absorbance standard curve of  $\text{Cr}^{3+}$ .

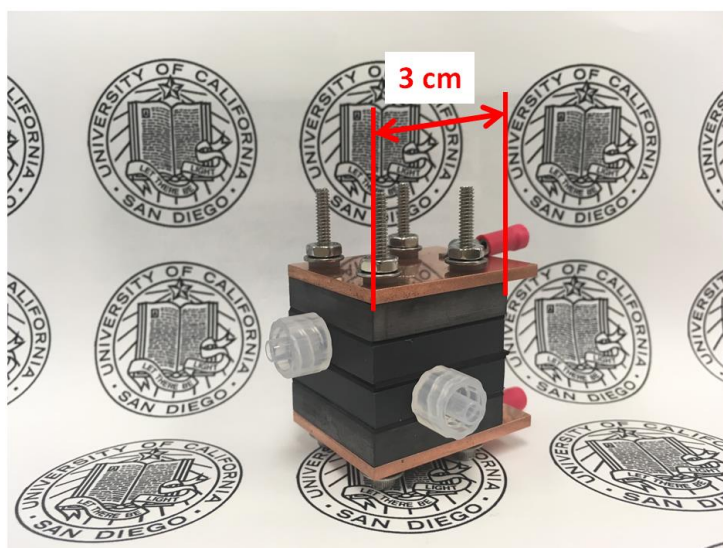


Figure S8. Photo of a flow battery hardware designed and fabricated in house.

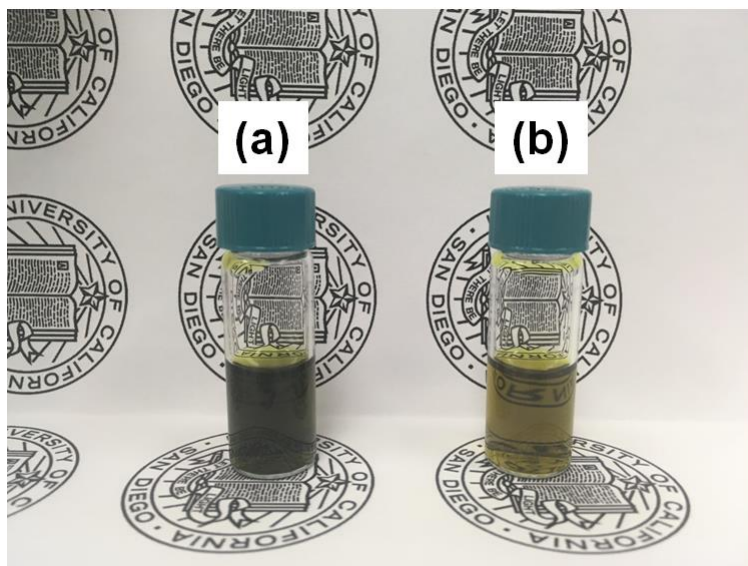


Figure S9. Photo of catholytes of flow batteries after cycling for 50 hours at the current density of  $20 \text{ mA cm}^{-2}$  and the flow rate of  $5 \text{ ml min}^{-1}$ : (a) Nafion, (b) h-DNf/oxide.

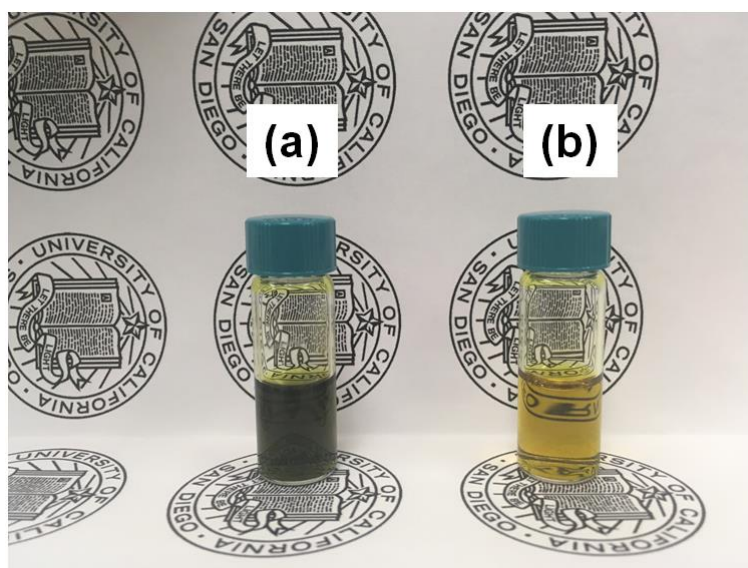


Figure S10. Photo of catholytes of flow batteries with no applied current density after 70 hours at the flow rate of  $5 \text{ ml min}^{-1}$ : (a) Nafion, (b) h-DNf/oxide.



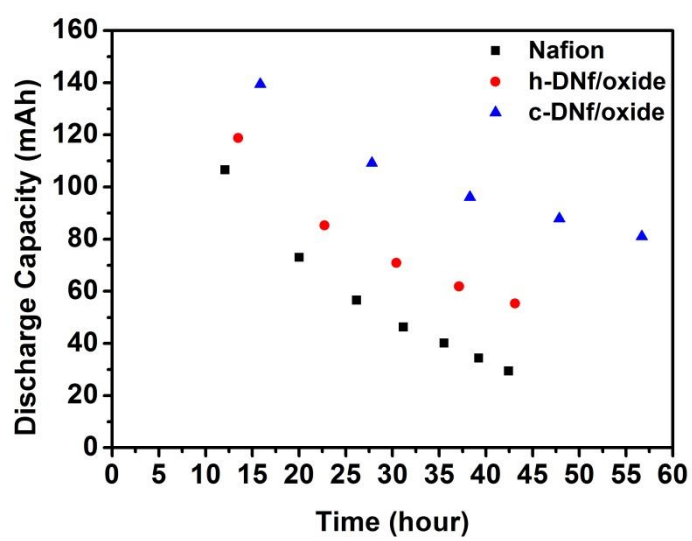


Figure S11. Capacity retention over time.