Supplemental Information

Poly (vinylene carbonate)-Based Composite Polymer Electrolyte with Enhanced Interfacial Stability to Realize High Performance Room-Temperature Solid-State Sodium Batteries

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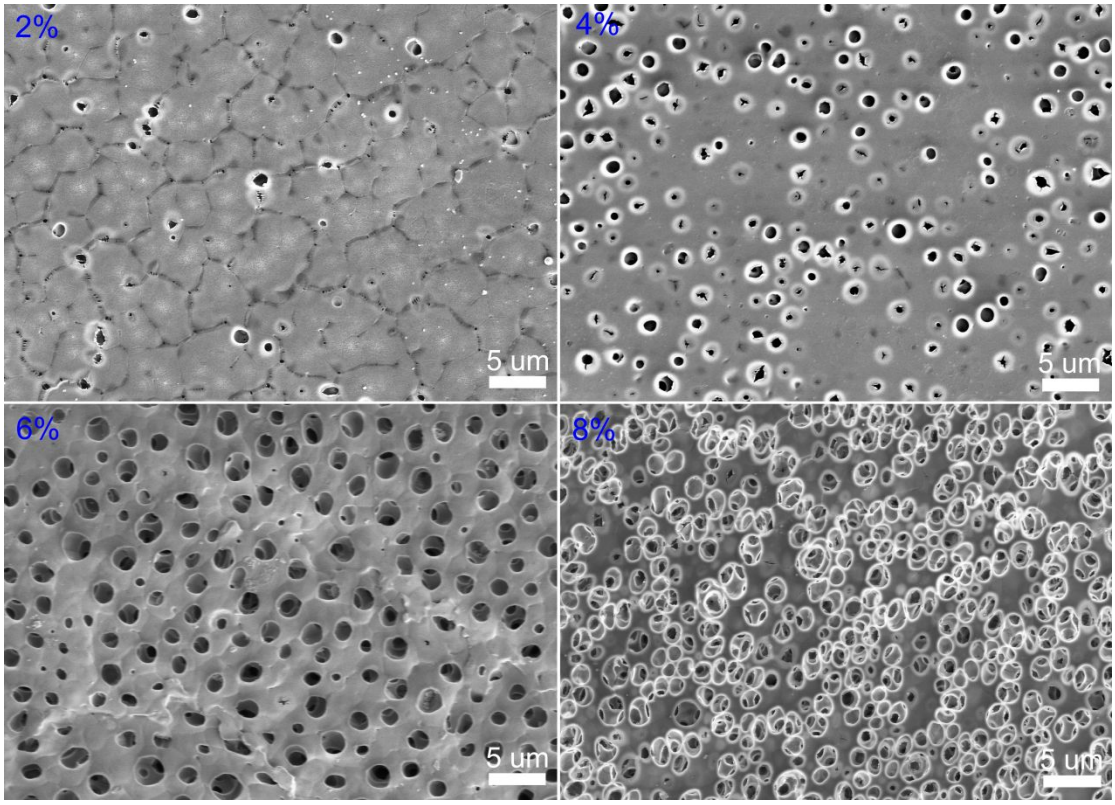

Figure S1. SEM images of PVdF-HFP porous supports with different non-solvent content.

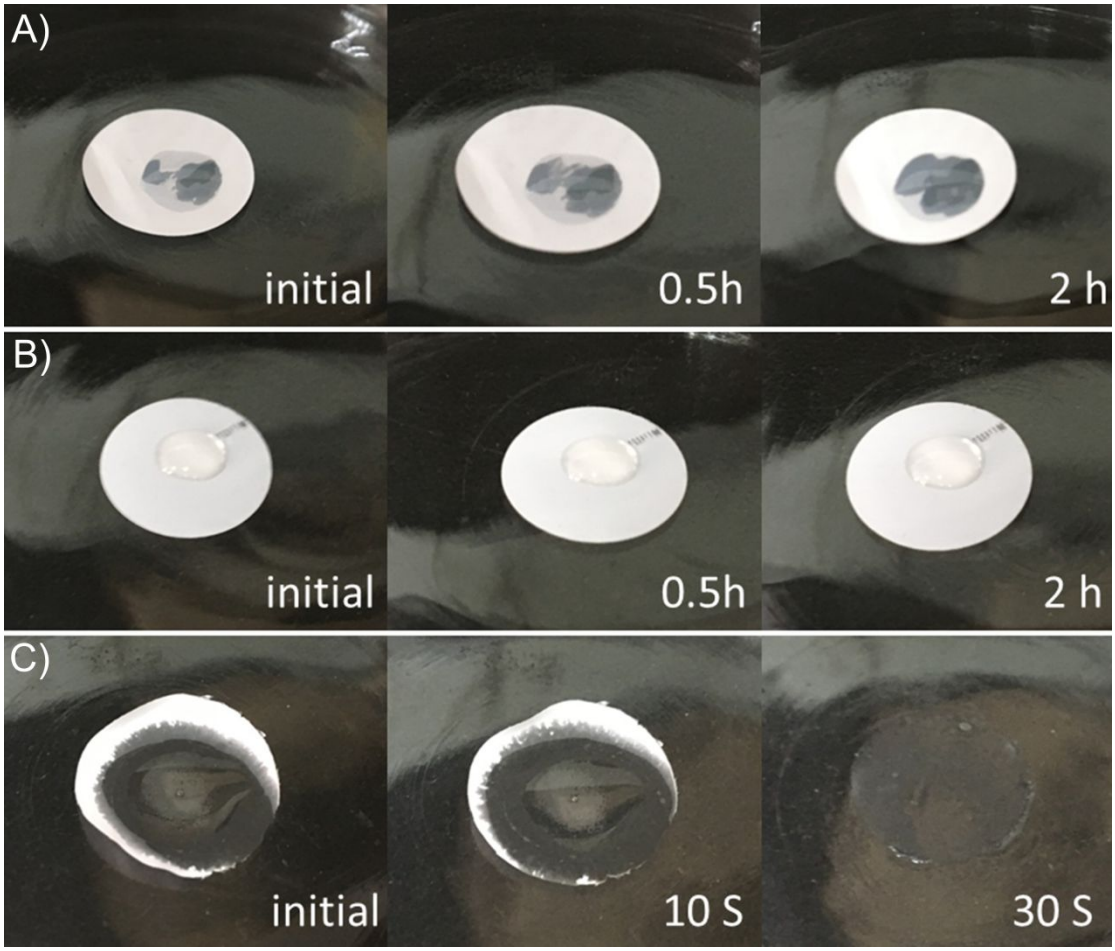

Figure S2. The comparison of wetting behavior of A) commercial PP separator, B) commercial PP/PE/PP separator and C) P-support surface with polymeric precursor solution during evolution time at room temperature.

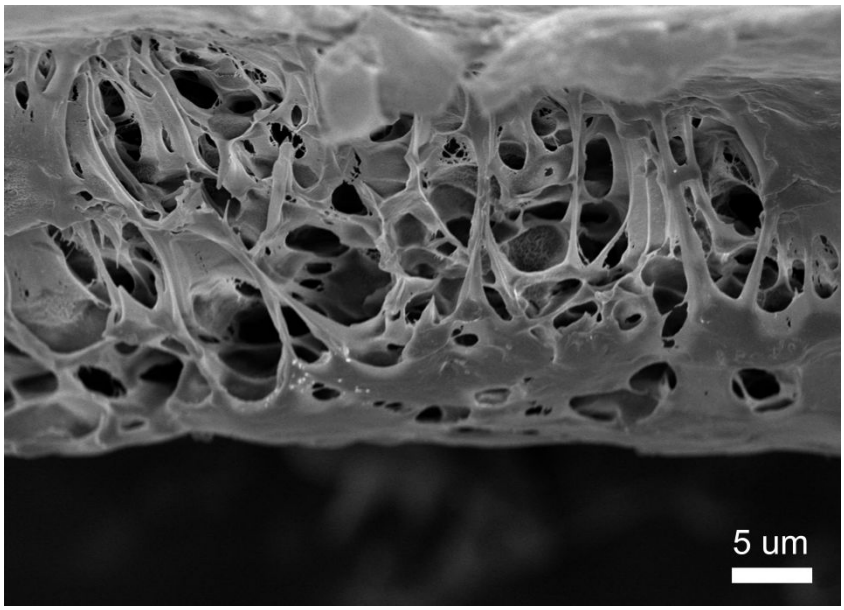

Figure S3. SEM image of the cross sectional view of pristine P-support membrane.

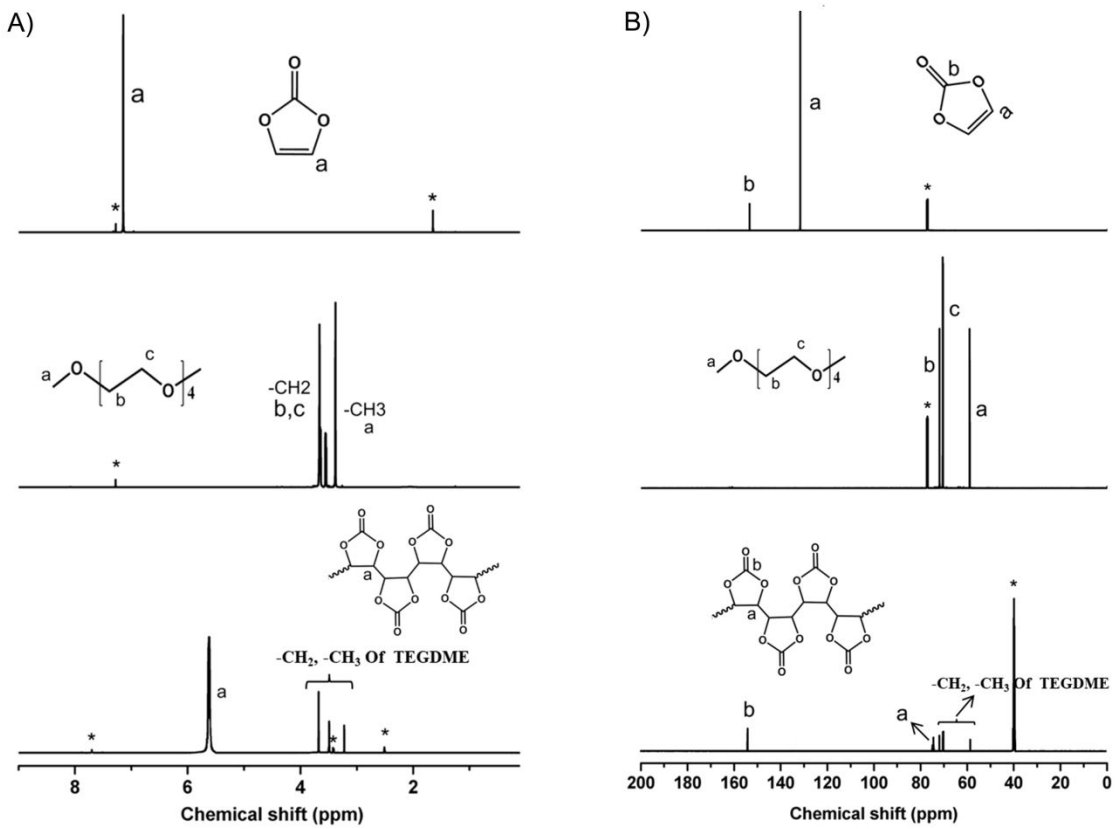

Figure S4. ^{1}HNMR A) and ^{13}C-NMR B) spectra of VC, TEGDME and polymer matrix of PVC-CPE. ^{1}HNMR and ^{13}C-NMR of VC and TEGDME in $CDCl_3$, HNMR and ^{13}C-NMR of polymer matrix in DMSO-d_6.

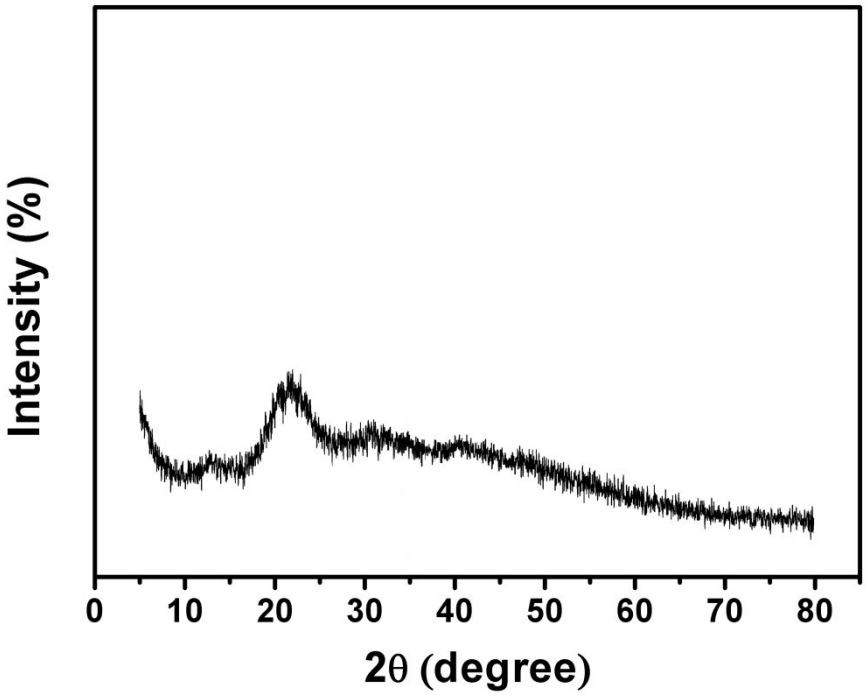

Figure S5. XRD pattern of PVC-CPE.

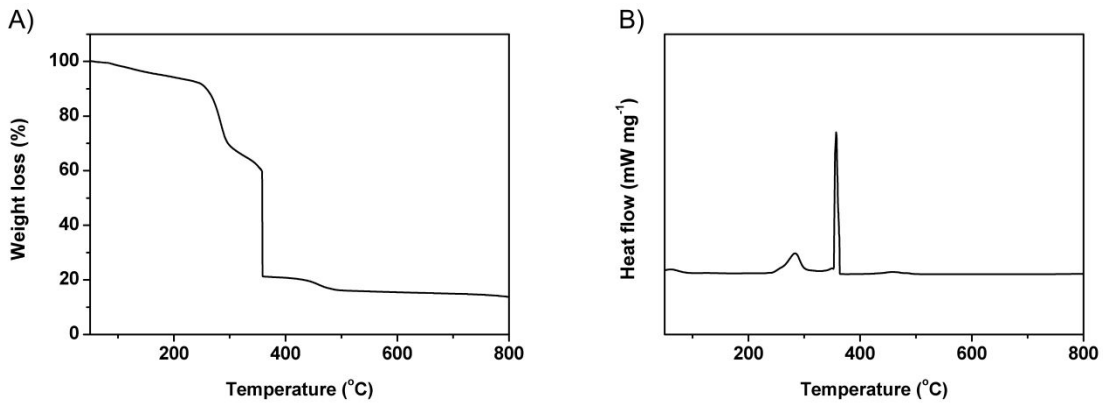

Figure S6. TGA A) and DSC B) profiles of PVC-CPE.

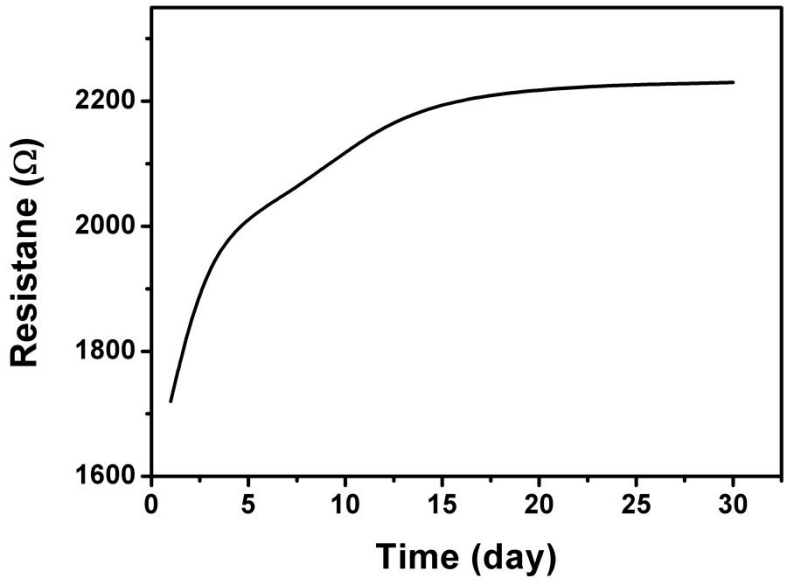

Figure S7. Time evolution of the interfacial resistance of Na/PVC-CPE/Na cell at room temperature.

Table S1. Ionic conductivity comparison of various solid electrolytes.

Author	Materials	Temperature (℃)	Ionic conductivity （S/cm）
Michel Armand et al.[1]	PEO/SiO_2–PEG–anion composite electrolyte	25	2.0×10^{-5}
P. Balaji Bhargav et al.[2]	PVA-NaBr (70:30)	30	1.362×10^{-6}
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V. M. Mohan et al.[3]	PEO-$NaLaF_4$ (70:30)	25	3.9×10^{-7}
K. Kiran Kumar et al.[4]	PEO:PVP:NaF (62.5:22.5:15)	30	1.17×10^{-7}
S. Selladurai. et al.[5]	PEO-$NaClO_3$	35	3.4×10^{-6}
S. Selladurai. et al.[5]	PEG-PEO-$NaClO_3$	35	3.07×10^{-5}
C Gerbaldi et al.[6]	PEO:$NaClO_4$:Na-CMC	25	$<10^{-6}$
Yong-Sheng Hu et al.[7]	NZMSP–PEO_{12}–NaFSI composite electrolyte	25	4.4×10^{-5}
Andrea Boschin et al.[8]	NaTFSI-$(PEO)_9$	20	4.5×10^{-6}
Aninda J. Bhattacharyya et al.[9]	PEO–$NaCF_3SO_3$-SN	25	1.1×10^{-4}
Yong-Sheng Hu et al.[10]	PEO-NaTFSI-50wt% NASICON	30	6.0×10^{-5}
This work	PVC-CPE	25	**1.2×10^{-4}**

Table S2. Sodium transference numbers of PVC-CPE at room temperature.

Sample	I_0 (μA)	I_s (μA)	R_0 (kΩ)	R_s (kΩ)	ΔmV	t_{Na^+}
PVC-CPE	1.32	0.98	1.95	01.98	10	0.60

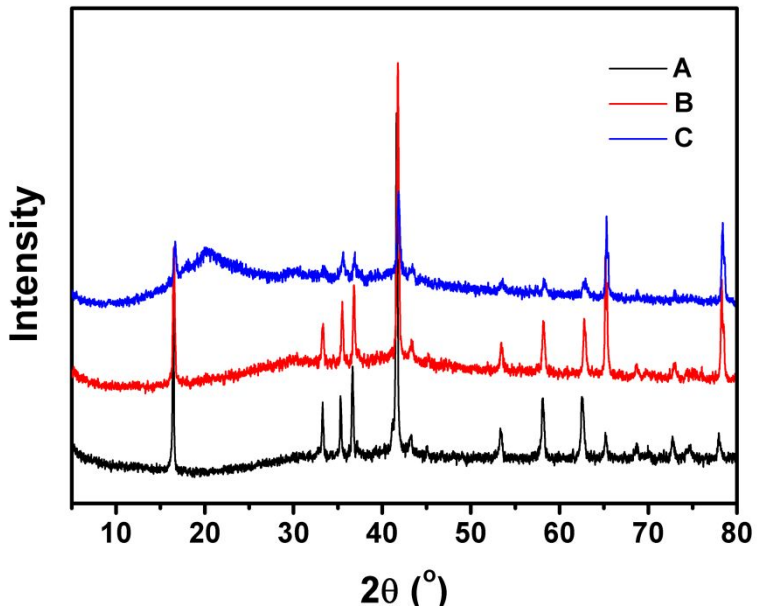

Figure S8. XRD patterns of A) NFM active material, B) original NFM electrode and C) c-NFM electrode.

Figure S9. Digital photograph of wetting behavior of original NFM electrode with the polymeric precursor solution.

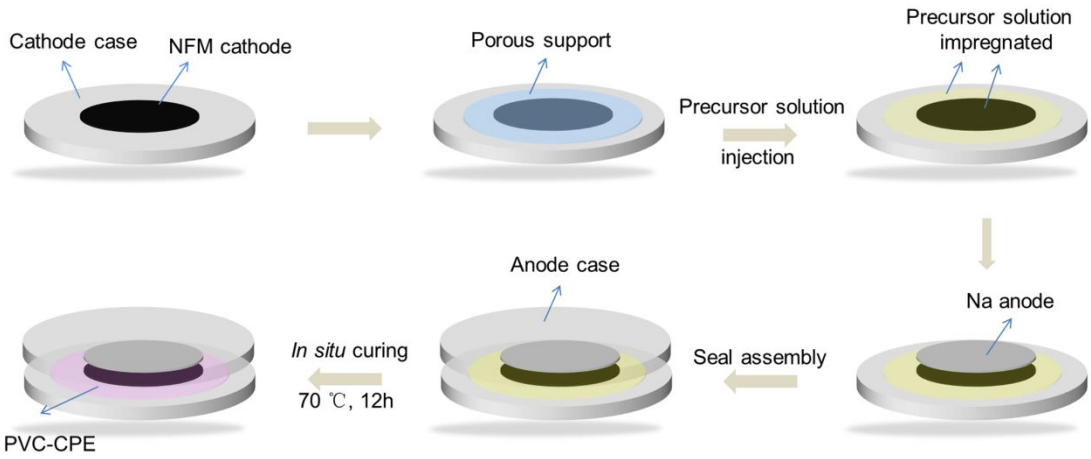

Figure S10. The preparation of c-NFM/PVC-CPE/Na solid-state battery by one-step *in situ* solidification method.

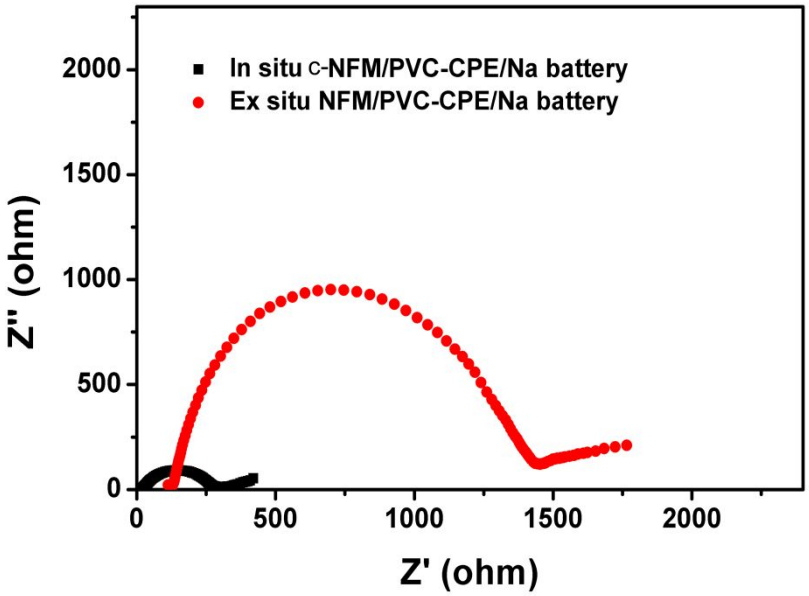

Figure S11. The EIS spectra for the *in situ* c-NFM/PVC-CPE/Na and *ex situ* NFM/PVC-CPE/Na batteries.

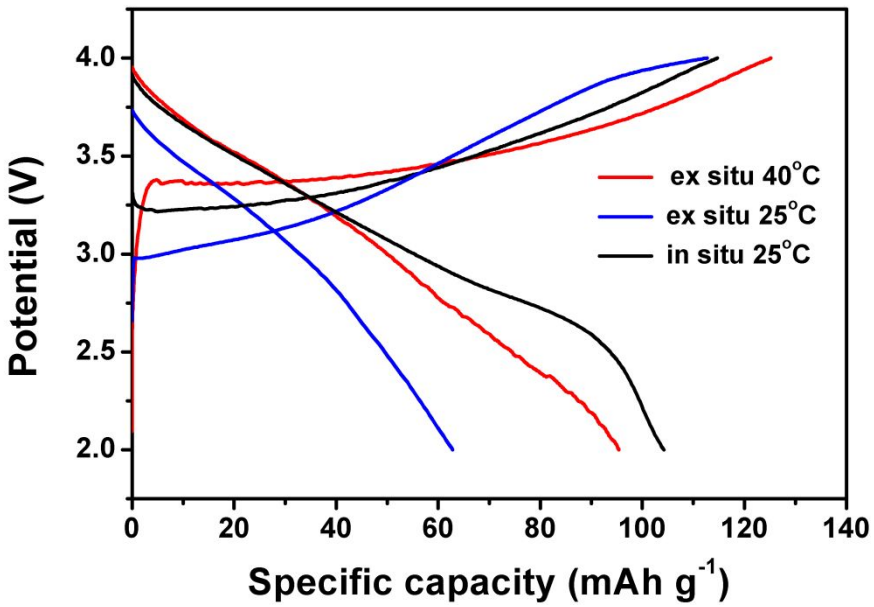

Figure S12. The comparison of initial charge and discharge curves of *in situ* c-NFM/PVC-CPE/Na cell and *ex situ* NFM/ PVC-CPE/Na cell at room temperature and 40 ℃ at 0.2 C.

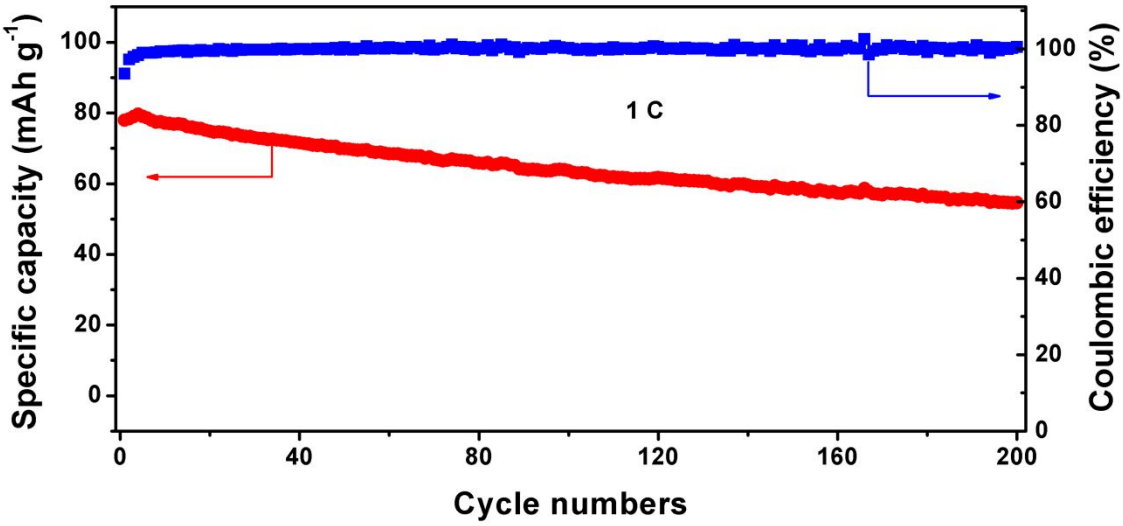

Figure S13. Cycling performance of *in situ* c-NFM/PVC-CPE/Na cell at a charge/discharge current density of 1 C at room temperature.

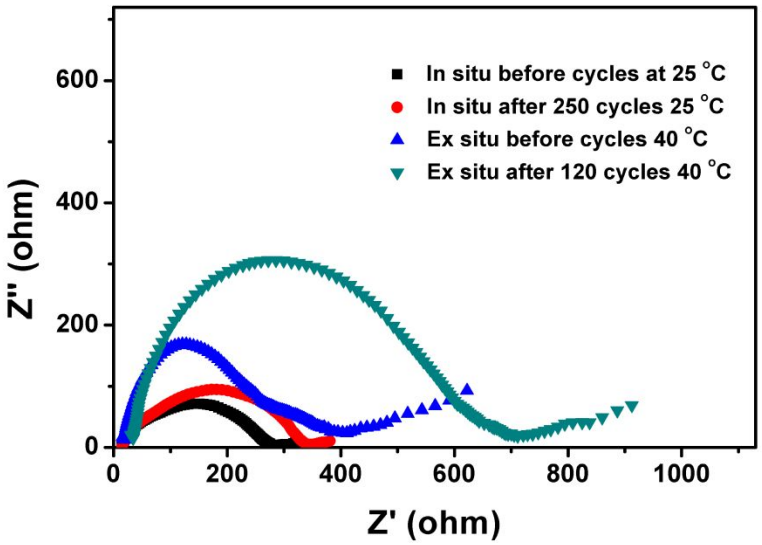

Figure S14. Nyquist plots of the *in situ* c-NFM/PVC-CPE/Na cell measured before and after 250 cycles at 0.2 C, 25 ℃ and *ex situ* NFM/ PVC-CPE/Na cell measured before and after 120 cycles at 0.2 C, 40 ℃ of operation.

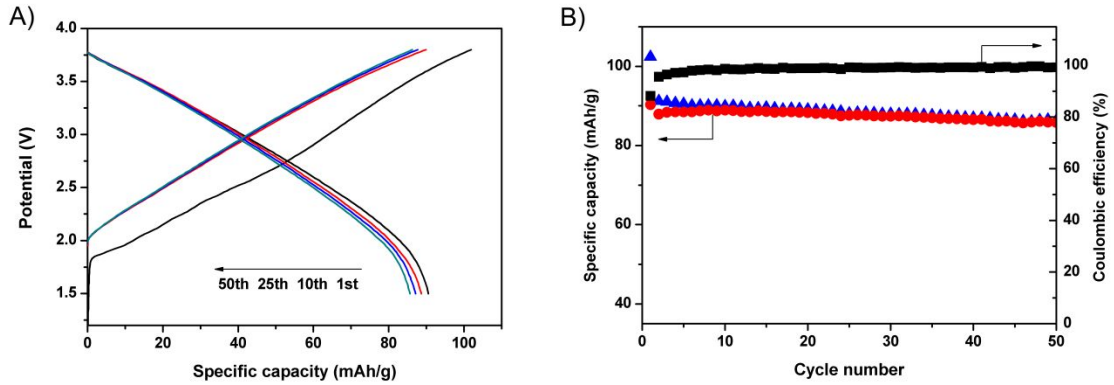

Figure S15. The charge/discharge profiles A) and cycling stability B) of c-NFM/PVC-CPE/hard carbon full cell at 0.2 C, at room temperature.

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