

Supporting information

NaBH₄-Poly(ethylene oxide) Composite Electrolyte for All-Solid-State Na-Ion Batteries

Xiaoxuan Luo,^a Kondo-Francois Aguey-Zinsou^{,b}*

^a MERLin, School of Chemical Engineering, The University of New South Wales, Sydney NSW 2052, Australia,

^b MERLin, School of Chemistry, University of Sydney, Sydney NSW 2006, Australia.

* f.aguey@sydney.edu.au

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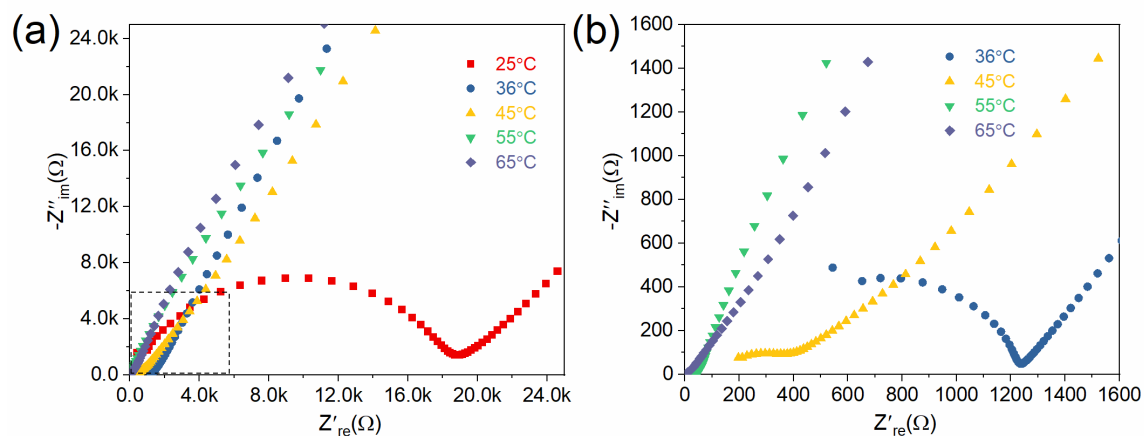


Figure S1. (a) Nyquist plots of Hy-NaBH₄-20PEO from 25°C to 65°C. (b) magnification of the dash box in Figure S1(a).

At room temperature, the Nyquist plot consists of a semicircle and line tail consistent with that of the reported borohydride-based electrolytes.¹ R is the intercept of semicircle with the X axis. With temperatures increasing, the magnitude of the semicircle gradually decreases.

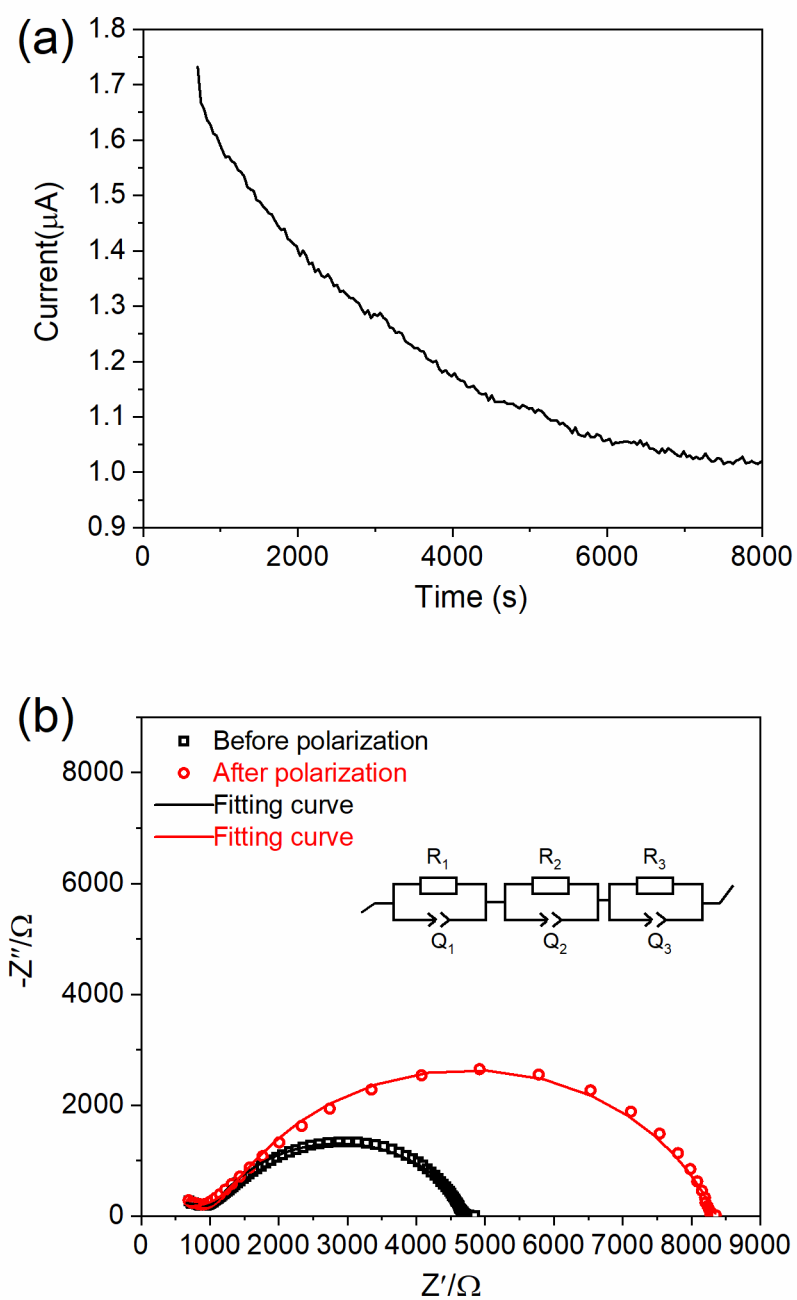


Figure S2. Current -time curves following DC polarization of Hy-NaBH₄-20PEO with 10 mV polarization voltage at 45 °C. (b) The Nyquist plot of Hy-NaBH₄-20PEO before and after DC polarization. The equivalent circuit was shown as insert.

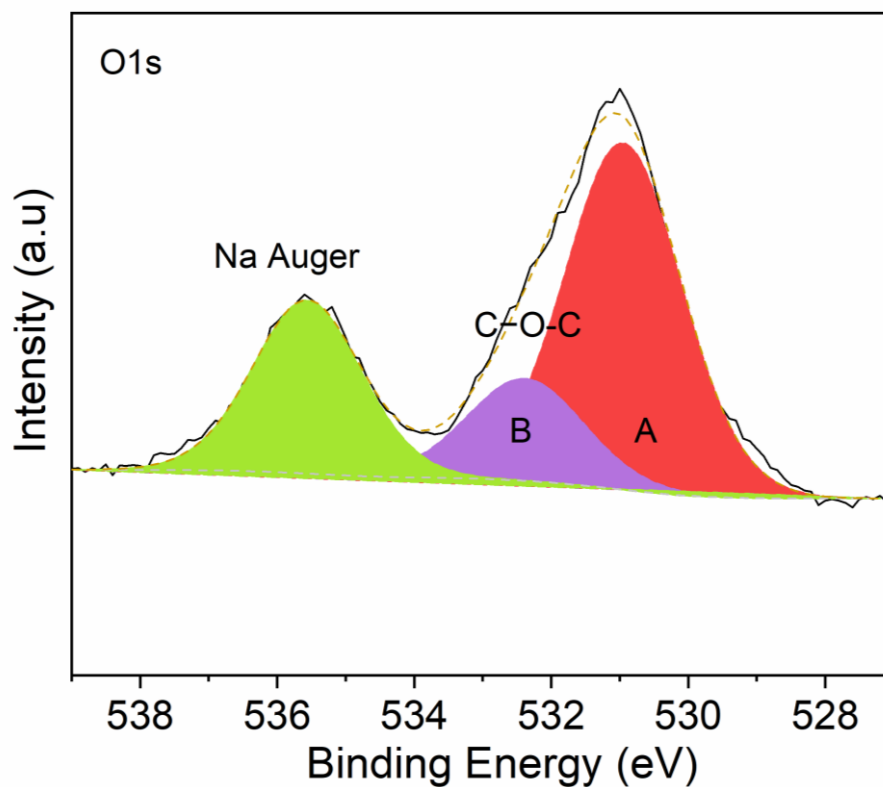


Figure S3. O1s XPS spectra of Hy-NaBH₄-20PEO.

The peak B located at 532.3 eV is assigned to the C-O-C from PEO.² The peak A may relate to the boron-oxide species,³ which is consistent with 191.2 eV in B1s spectrum (Figure 3a).

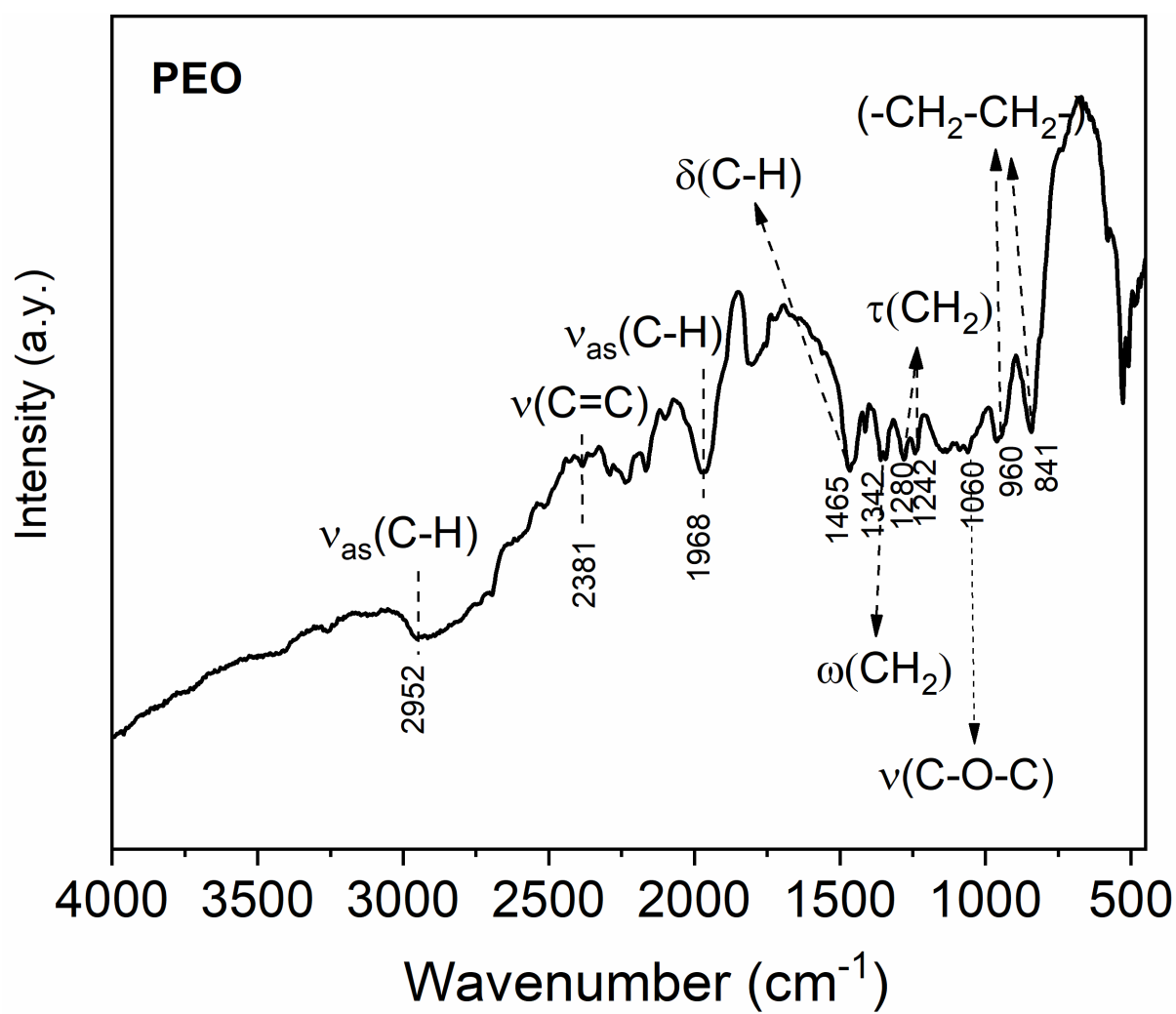


Figure S4. FTIR of PEO

Table S1 the lattice paraterm of NaBH₄ in Hy-NaBH₄-PEO calculated from XRD by Retvield analysis

Materials	Lattice parameter a ($\pm 0.001 \text{ \AA}$)
Unmodified NaBH ₄	6.164
Hy- NaBH ₄ -5PEO	6.163
Hy- NaBH ₄ -10PEO	6.157
Hy- NaBH ₄ -20PEO	6.160
Hy- NaBH ₄ -30PEO	6.159

Table S2. The degeed of crystallinity (χ_c) of PEO in Hy-NaBH₄-PEO calculated by using melting enthalpy in DSC.

Materials	Degree of crystallinity (χ_c)
PEO	35.5%
Hy- NaBH ₄ -5PEO	10.7%
Hy- NaBH ₄ -10PEO	18.8%
Hy- NaBH ₄ -20PEO	20.8%
Hy- NaBH ₄ -30PEO	21.6%

Table S3. Na⁺ transference number (t_{Na^+}) of Hy-NaBH₄-20PEO.

Materials	$I_{(t=0)}/\mu A$	$I_{(t=\infty)}/\mu A$	$R_{(t=0)}/\Omega$	$R_{(t=\infty)}/\Omega$	t_{Na^+}
Hy-NaBH ₄ -20PEO	1.73	1.0	3630	6569	0.54

$$t_{Na^+} = \frac{I_{\infty}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\infty} R_{\infty})}$$

Table S4. Summarized of PEO composite sodium solid state electrolytes

Materials	Ionic conductivity (S cm ⁻¹)	Transference number	Ref
PEO-NaPF ₆	6.3 × 10 ⁻⁴ @ 80 °C	0.58	4
PEO-NaClO ₄ - Na ₃ Zr ₂ Si ₂ PO ₁₂	7.8 × 10 ⁻⁴ @ 75 °C	NA	5
Na ₃ PS ₄ -PEO	9.5 × 10 ⁻⁴ @ 25 °C	NA	6
Na ₃ Zr ₂ Si ₂ PO ₁₂ - PEO ₁₂ -NaFSI	2.2 × 10 ⁻⁵ @ 25 °C	NA	7
PEO ₂₀ :NaTFSI	1.1 × 10 ⁻³ @ 80 °C	0.39	8
Hy-NaBH ₄ -20PEO	1.6 × 10 ⁻³ @ 45 °C	0.54	This work

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