

Supporting Information

Ether-Water Hybrid Electrolyte Contributing to Excellent Mg Ion Storage in Layered Sodium Vanadate

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The calculation process of the diffusion coefficient and capacitive-controlled ratio:

Generally, the peak currents and the scan rates have the association exhibited below:

$$i = av^b \quad (1)$$

Which can also be expressed as:

$$\log(i) = b \log(v) + \log(a) \quad (2)$$

Where i is the peak current (A), a and b are adjustable parameters, v is the relevant scan rate ($V s^{-1}$). The b value can be acquired from the linear relation between $\log(i)$ and $\log(v)$ of the redox peaks.

Furthermore, the contribution of a capacitive process and a diffusion-limited redox process in whole capacity can be deconvoluted through the following formula: ⁴¹

$$i = k_1 v + k_2 v^{\frac{1}{2}} \quad (3)$$

which can be reformulated as:

$$\frac{i}{v^{\frac{1}{2}}} = k_1 v^{\frac{1}{2}} + k_2 \quad (4)$$

where i depicts the current response, $k_1 v$, represents the capacitive contribution, and $k_2 v^{\frac{1}{2}}$ presents diffusion-controlled contribution. The k_1 value can be acquired by fitting the $\frac{i}{v^{\frac{1}{2}}}$ vs. $v^{\frac{1}{2}}$ plots.

A sequence of current pulses followed by a relaxation process is executed on NVO cathode unless the cutoff voltage of 1.2 V vs. Ag/AgCl is achieved. The apparent diffusion coefficient (D) of Mg^{2+} in the NVO cathode material can be evaluated based on the following formula. ³⁹

$$D = \frac{4}{\pi\tau} \left(\frac{mV_m}{MS} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad (5)$$

where, m , M and V_m are the mass, molar mass, and molar volume of NVO, τ represents the constant current pulse duration, S is the electrode electrolyte interface area (here adopted as the geometric area of the electrode); ΔE_s is the steady state potential alteration by the current pulse; ΔE_τ is the potential alteration during the constant current pulse after removing the iR drop. ⁴⁴

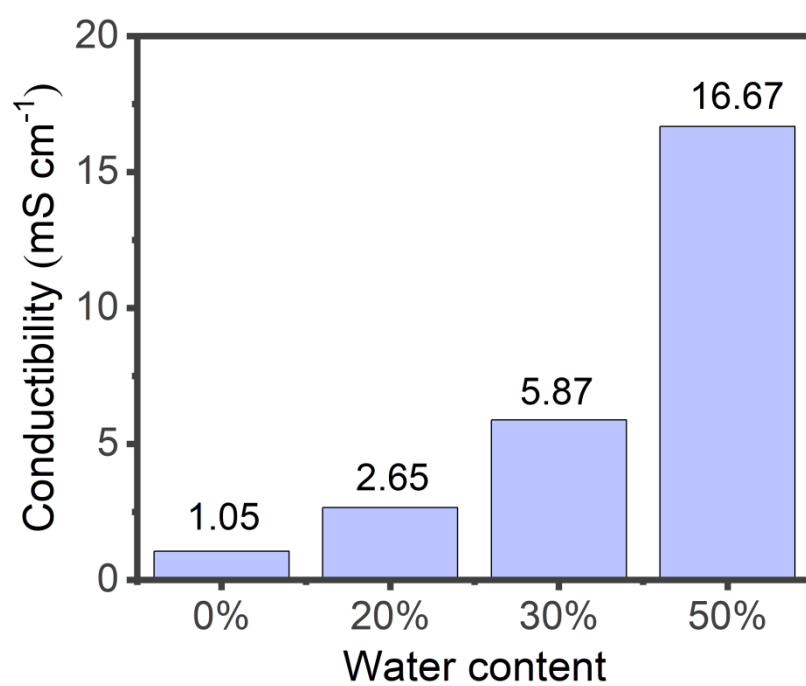


Figure S1 The ionic conductivity of ether-water hybrid electrolyte with different water content.

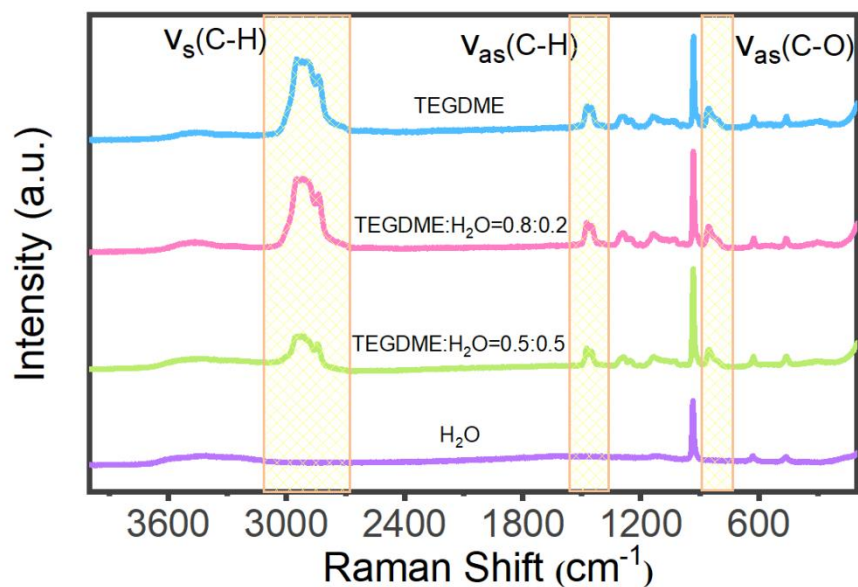


Figure S2 Raman spectra of ether-water hybrid electrolyte with different TEGDME and water content.

With increasing TEGDME portion in the electrolyte, the intensity of characteristic TEGDME molecule gradually increased, including the symmetrical stretching C–H bond at 2700–3100 cm^{-1} and the C–H asymmetric stretching vibration at 1400–1500 cm^{-1} .

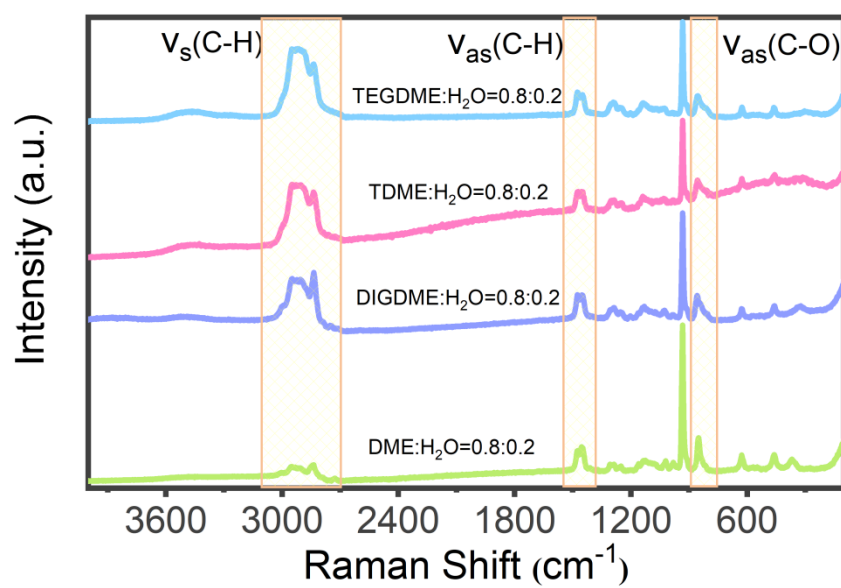


Figure S3 Raman spectra of Mg hybrid electrolyte with ethers of different chain lengths.

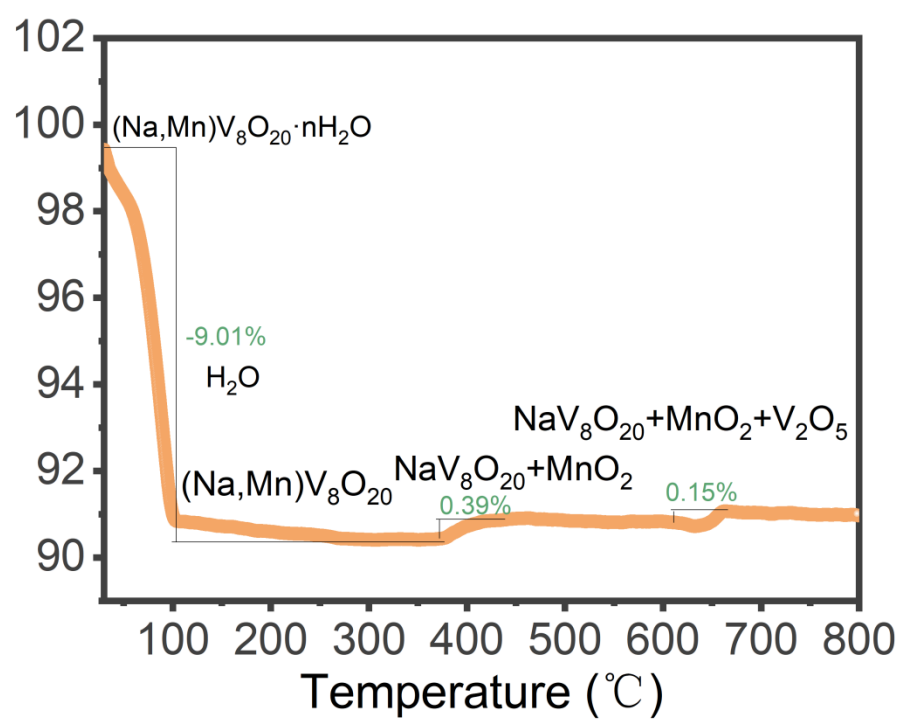


Figure S4 Thermogravimetric (TGA) curve of NVO samples.

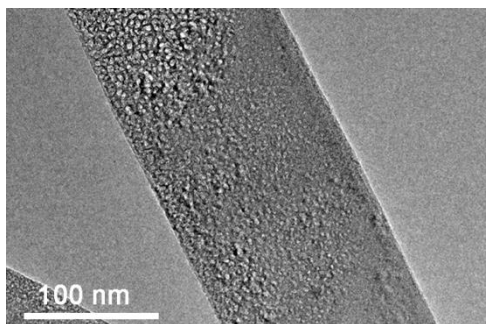


Figure S5 TEM image of the NVO sample

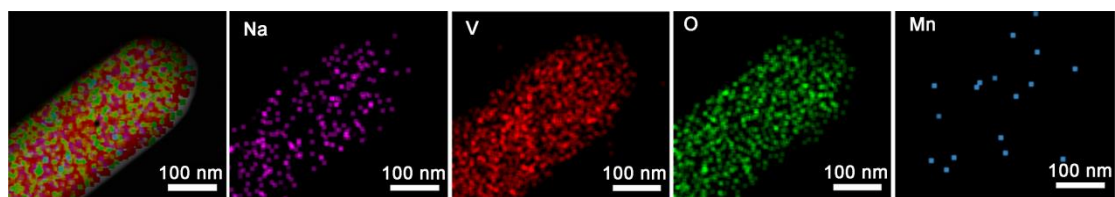


Figure S6 The corresponding TEM-EDX element mapping images of NVO samples.

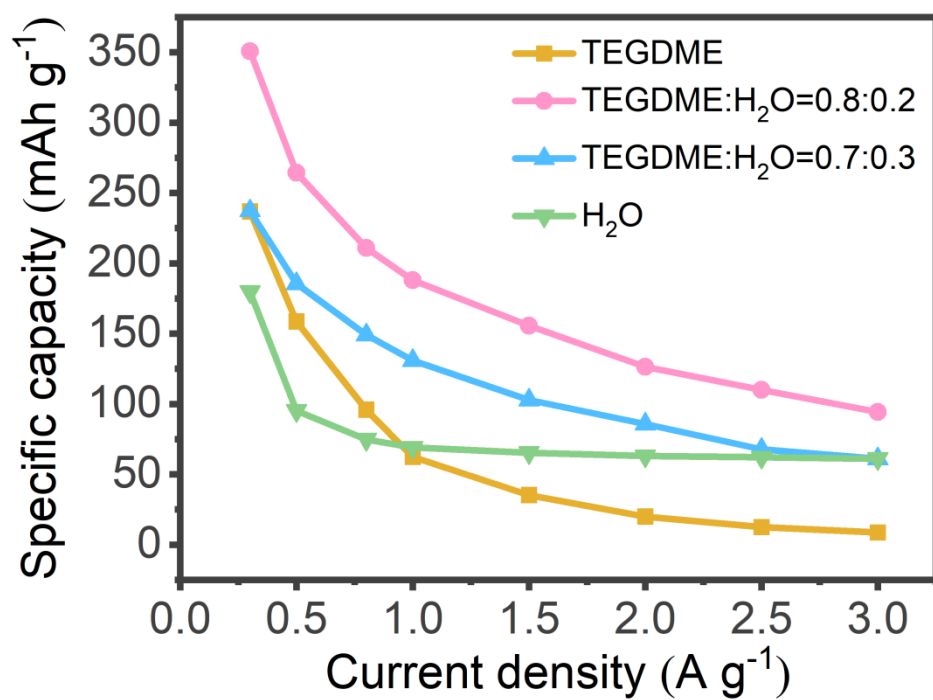


Figure S7 The specific capacities of the NVO cathode in Mg hybrid electrolyte with different water content at the different current density.

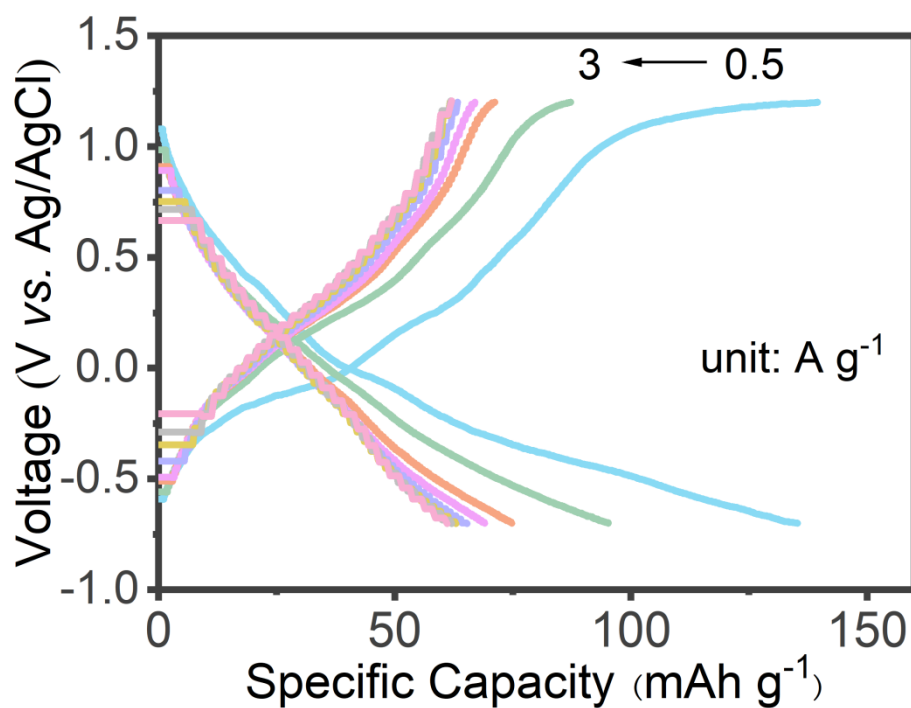


Figure S8 GCD curves of the NVO cathode in aqueous electrolyte measured using three electrode configuration. The platform appears at around 1 V during low-current charging is related to the oxygen evolution phenomenon.

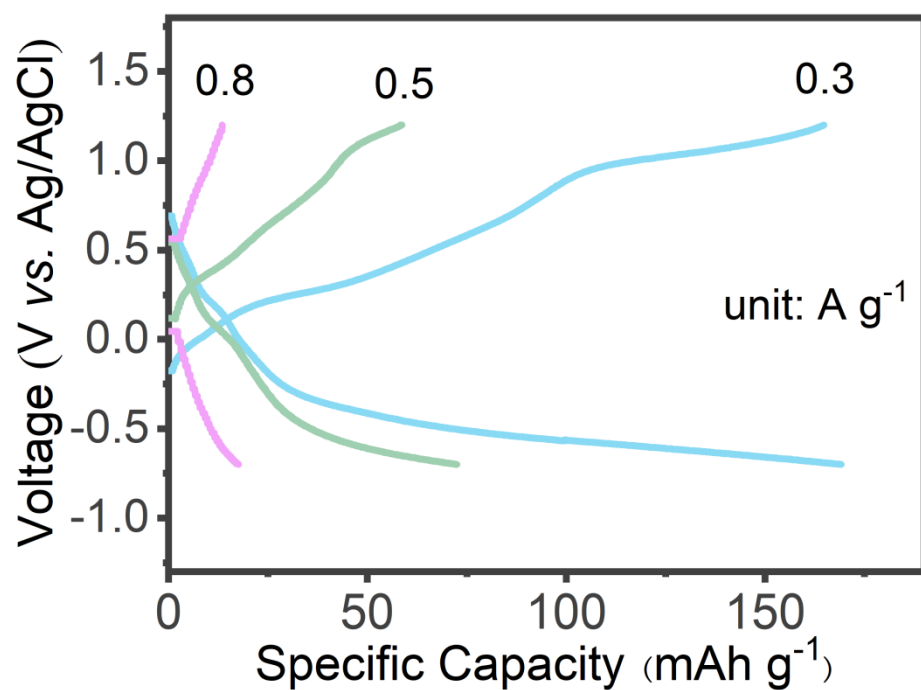


Figure S9 GCD curves of the NVO cathode in pure TEGDME electrolyte measured using three electrode configuration.

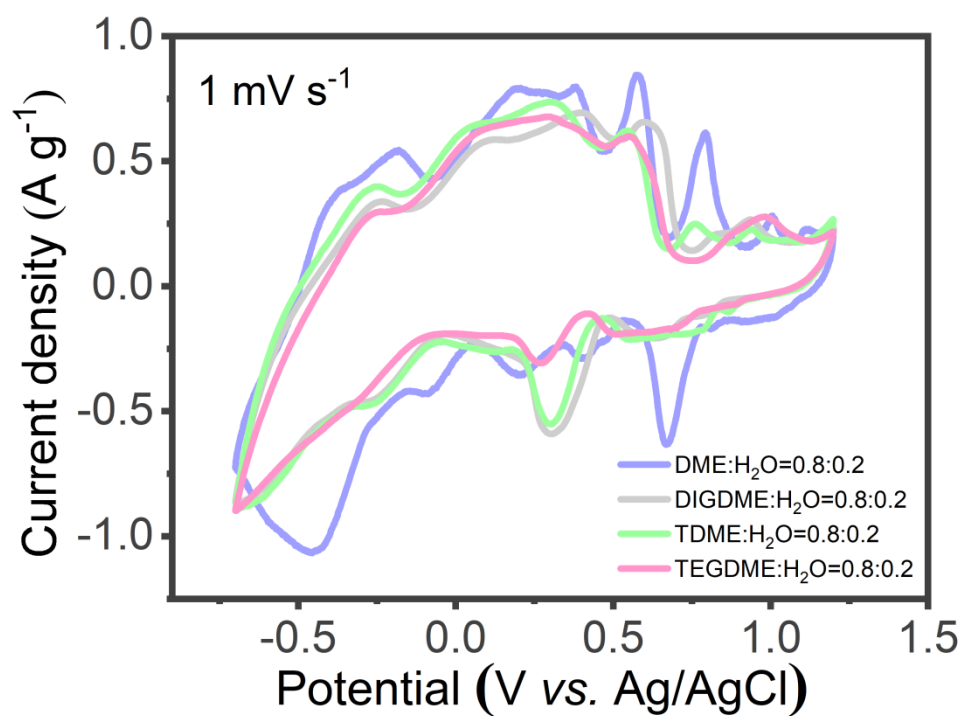


Figure S10 CV profiles of NVO in Mg hybrid electrolyte with ethers of different chain lengths at 1 mV s^{-1} .

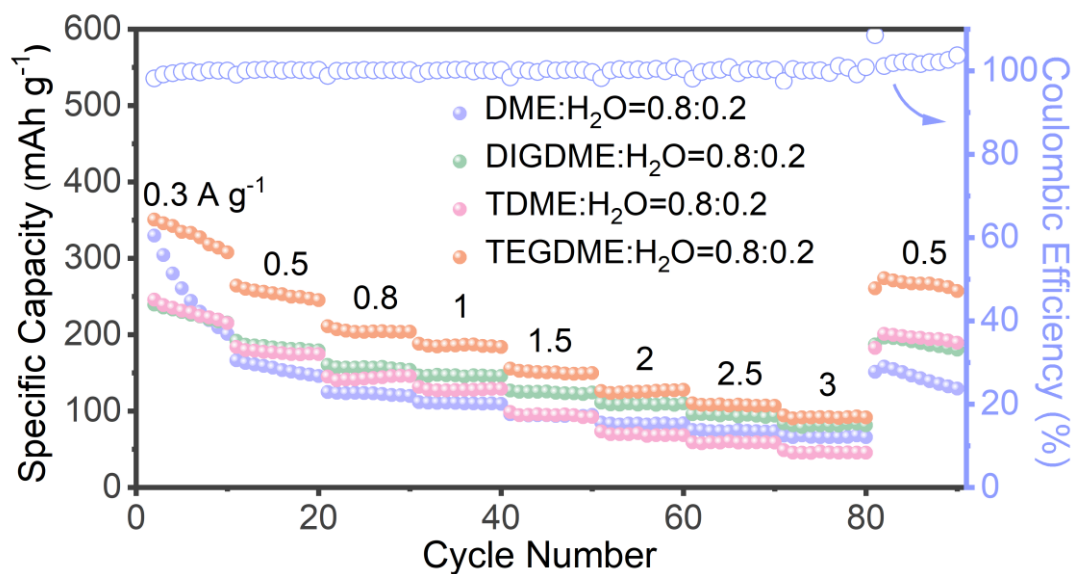


Figure S11 Rate performance for ether-water hybrid electrolytes of different chain lengths. The right axis is the corresponding Coulombic efficiency of TEGDME: H_2O =0.8:0.2.

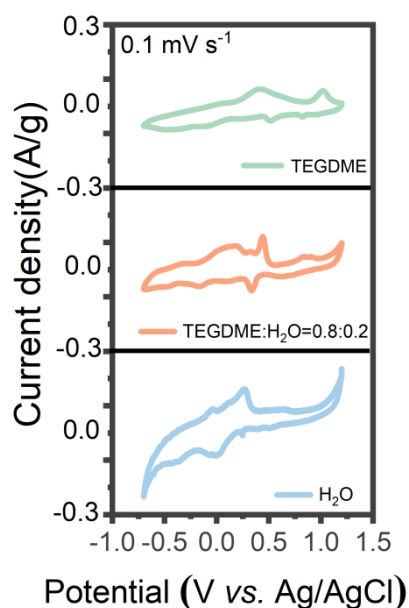


Figure S12 CV comparison of NVO cathode in TEGDME, TEGDME: H₂O=0.8:0.2, H₂O-based electrolyte at 0.1 mV s⁻¹.

It is seen that noticeable oxygen evolution phenomenon was observed at above 1 V vs. Ag/AgCl in pure water-based electrolyte, due to the narrow electrochemical stability window of aqueous electrolyte. In contrast, the addition of organic TEGDME solvent broadens the electrochemical stability window of the hybrid electrolyte and organic electrolyte, since the oxygen evolution phenomenon is not obvious, which consistent with the GCD curve shown in **Figure 2e** and **figure S9**.

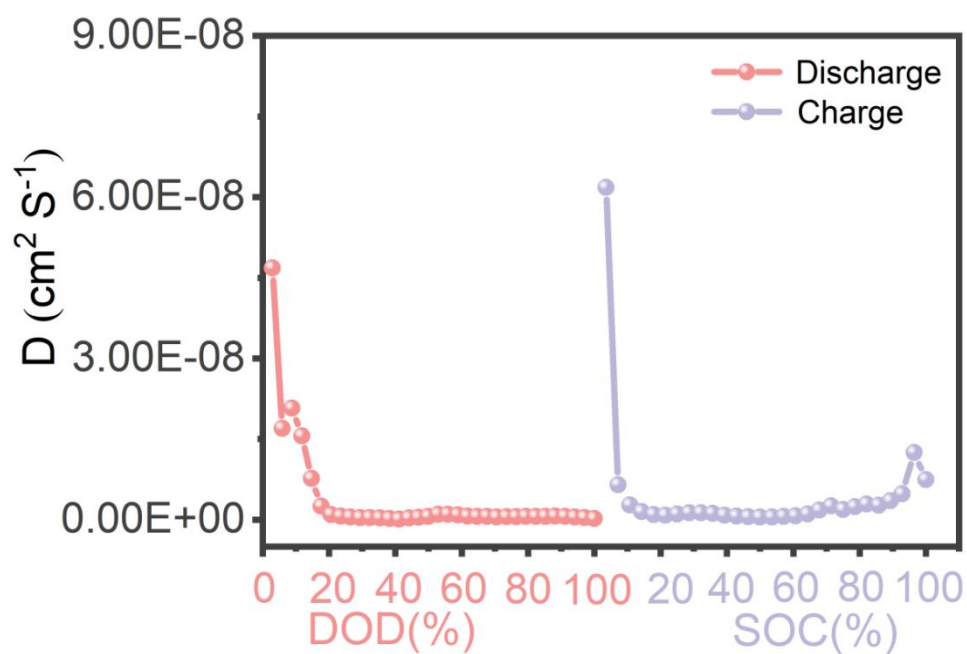


Figure S13 The diffusivity coefficient of Mg^{2+} in the discharge and charge processes of the NVO in pure organic electrolyte.

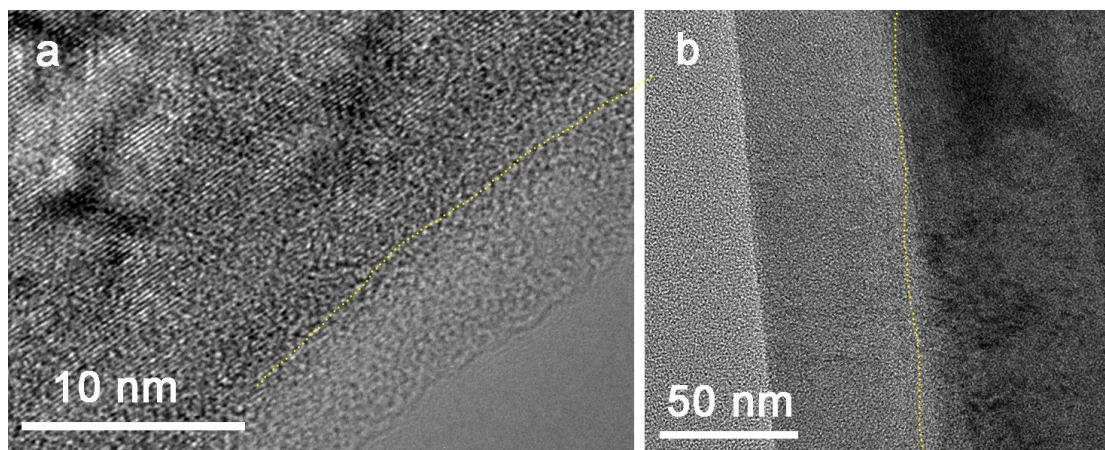


Figure S14 (a) TEM image of the CEI of NVO cathode at 1st discharge state in water-ether hybrid electrolytes. (b) TEM image of the CEI of NVO cathode at 40st discharge state in water-ether hybrid electrolytes.

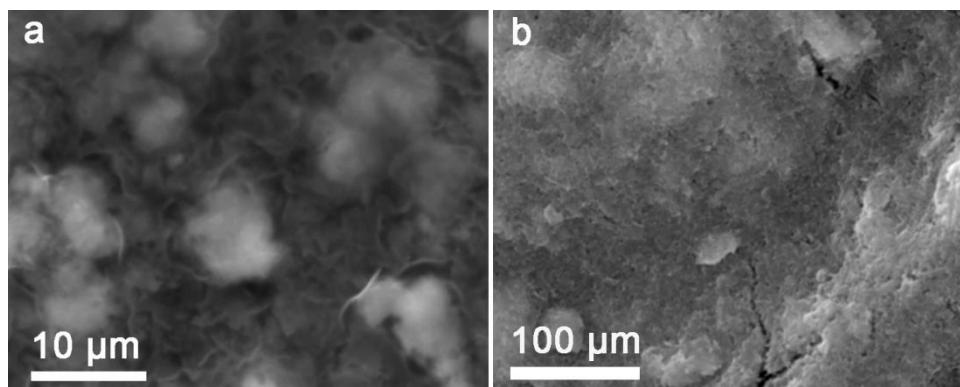


Figure S15 SEM images of NVO cathode after 1st discharge (a) in pure TEGDME electrolyte and (b) in pure H₂O electrolyte.

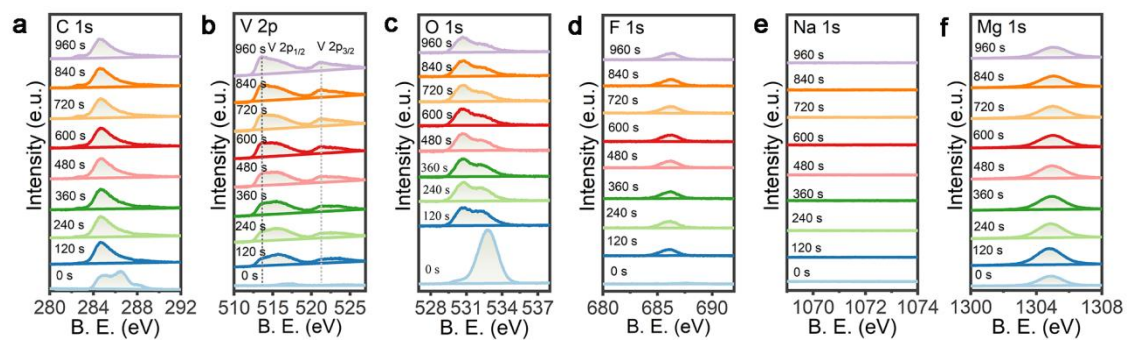


Figure S16 (a-f) XPS spectra of the 2nd charged state of NVO in Mg hybrid electrolyte, showing C 1s, V 2p, O 1s, F 1s, Na 1s and Mg 1s signals.

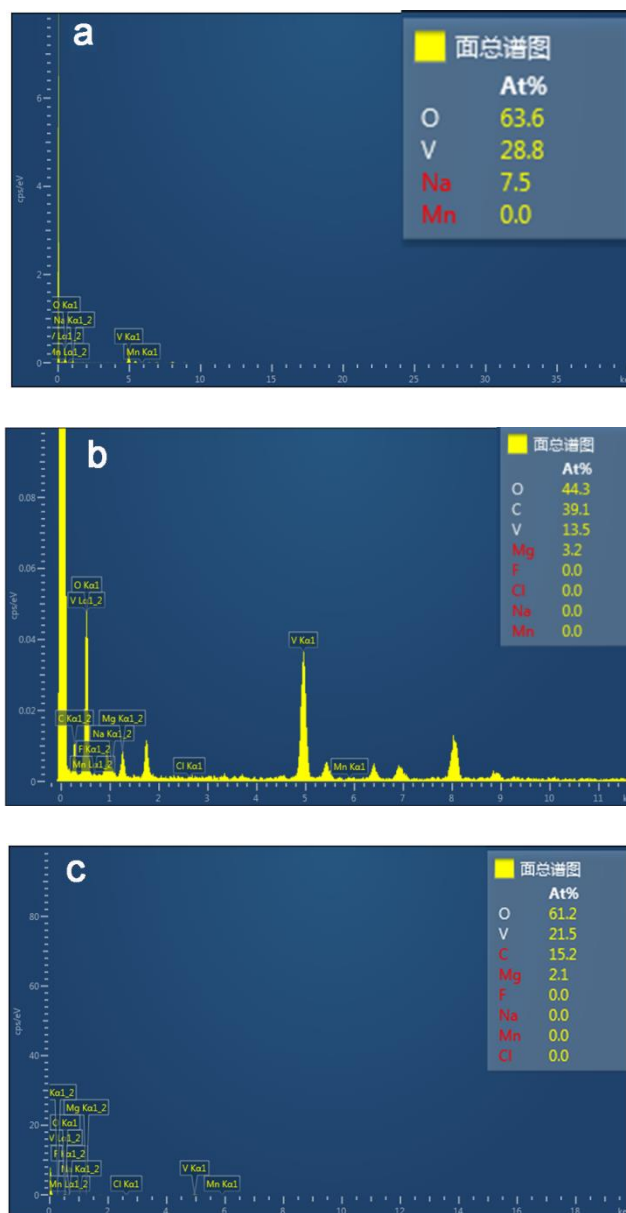


Figure S17 TEM-EDS element analysis on NVO cathode in different states: (a) initial (point 1), (b) 1st discharged (point 6), (c) 2nd charged state (point 10).

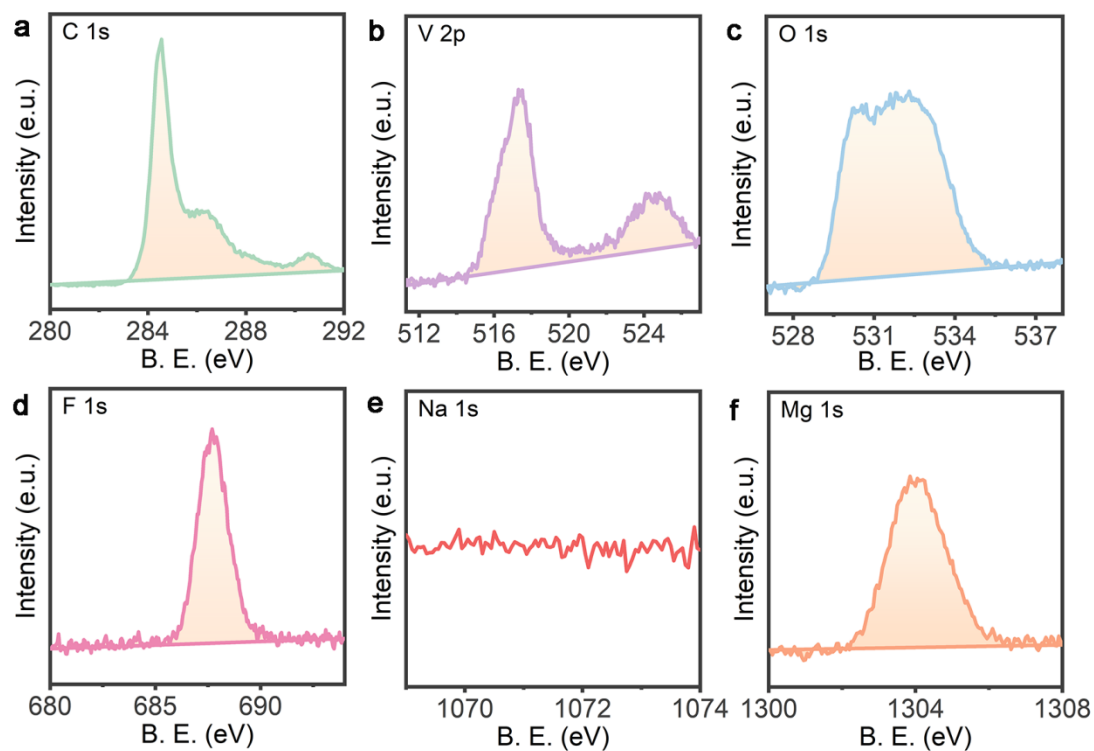


Figure S18 XPS of the 1st fully discharged NVO cathode in water-based electrolyte, showing C 1s, V 2p, O 1s, F 1s, Na 1s and Mg 1s signals. B.E. is the abbreviation of binding energy.

Table S1. Rietveld refinement parameters of Mn-doped NVO.

Space group		C 2/m (12)
lattice parameters	a (Å)	11.799(9)
	b(Å)	3.649(9)
	c(Å)	11.139(6)
	$\alpha(^{\circ})$	90
	$\beta(^{\circ})$	103.59(6)
	$\gamma(^{\circ})$	90
	Volume(Å ³)	466.33(1)
Fitting index	Rwp= 13.9%	
	Rp=9.6%	

Table S2. Performance comparison of NVO with reported cathode materials for MIBs.

Configuration	Working Electrode	Counter Electrode	Reference Electrode	Electrolyte	Specific capacity @current	Capacity retention/Cycle number/current	Ref.
Three electrode system	Mn-NVO	Pt	Ag/AgCl	1 M Mg(ClO) ₂ in TEGDME/H ₂ O	350.6 mAh g ⁻¹ @ 0.3 A g ⁻¹ 94.3 mAh g ⁻¹ @ 3 A g ⁻¹	81.7 mAh g ⁻¹ /1000/1.5 A g ⁻¹	This work
	V ₂ O ₅ ·0.4H ₂ O/graphite	Pt	SCE	10.2 mol (kg H ₂ O) ⁻¹ Mg(NO ₃) ₂ /H ₂ O	102 mAh g ⁻¹ @1 A g ⁻¹ 44 mAh g ⁻¹ @5 A g ⁻¹	80 mAh g ⁻¹ /10/1 A g ⁻¹	26
	Spinel Li _x Mn ₂ O ₄ (x ≈ 0.2)	Pt	SCE	1 M Mg(NO ₃) ₂ /H ₂ O	190 mAh g ⁻¹ @0.014 A g ⁻¹	/	27
Two electrode system	NaV ₂ (PO ₄) ₃	AC	/	0.3 M Mg(TFSI) ₂ /AN	95.3 mAh g ⁻¹ @0.02 A g ⁻¹	77.2 mAh g ⁻¹ /100/0.02 A g ⁻¹	28
	2H-MoS ₂	Mg	/	0.4 M MgBOR/DME	118 mAh g ⁻¹ @0.01 A g ⁻¹ 150 mAh g ⁻¹ @0.5 A g ⁻¹	56 mAh g ⁻¹ /100/0.1 A g ⁻¹	29
	V ₂ O ₅ ·nH ₂ O	Sn	/	1 M Mg(ClO ₄) ₂ /AN	160 mAh g ⁻¹ @0.02 A g ⁻¹	~120 mAh g ⁻¹ /50/0.03 A g ⁻¹	30
	NaV ₃ O ₈	AC	/	0.5 M Mg(ClO ₄) ₂ /AN	204.2 mAh g ⁻¹ @0.1 A g ⁻¹	160 mAh g ⁻¹ /100/1 A g ⁻¹	31