Electronic Supplementary Information

Towards Durable Li-Hybrid Flow Battery: Composite Membrane Development, Cell Performance, and Perspective

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Section S1. Additional experimental details (*Fig. S1-S2*)

LATP Filler Preparation

Li₂CO₃ (≥99%, Sigma-Aldrich, Chile), NH₄H₂PO₄ (≥98%, Alfa Aesar, Japan), Al₂O₃ (decomposed from Al(NO₃)₃·9H₂O, ≥97%, RusChem, Russia), and TiO₂ (≥99.5%, Sigma-Aldrich, Germany) were stoichiometrically mixed (Li₂CO₃ was taken with the 5% excess — the losses are expected at high temperatures), milled manually in agate mortar with addition of iso-propanol, and calcined at 750 °C for 3 h (14 h ramp) in a muffle furnace (Nabertherm L5/12/P330, Germany) in an alumina crucible with the application of the burnable separator.¹ Next, a sintered ceramic chunk was manually milled with iso-propanol, mixed with 5 wt.% polyethylene glycol (PEO, M_w ~1500, MO, USA) added as an iso-propanol solution during the subsequent additional milling procedure. The powder was then, pressed (Carver 4350.L, IN, USA) into 0.5-g pellets, which were placed in an alumina crucible and annealed at 850 °C for 3 h (14 h ramp). Final pellets were air-quenched and thrown on the aluminum foil to complete and preserve the NASICON phase formation. LATP ceramics were further applied for the composite fabrication immediately or placed inside the Ar glove box and sealed in a pouch for delayed use. The further membrane fabrication initiates with the LATP filler preparation: manual grinding of an as-synthesized or just unsealed 0.5-g ceramic pellet in the agate mortar with the following intense milling in the high-energy shaker (SPEX 8000, NJ, USA) for 1.5 h.

LATP Structure Refinement

We collected the membrane patterns up to 80 degrees: these samples exhibit stronger intensity fade at higher angles and a wider range was considered unnecessary. The shortened range impacted data accuracy, which was thoroughly represented and taken into account for further consideration and comparative analysis.

The LeBail refinement settings — zero shift and asymmetry factors — were established by the registration, profile and structural analysis of Al_2O_3 NIST 676a standard as described in Ref.² The LeBail refinement settings were as follows: background — manual in combination with the Chebyshev polynomial with 5 variables; unit cell dimensions *a* and *c*; profile — Pseudo-Voigt peak-shape function with *GW*, *LY*, anisotropic strain broadening — tensor approach accompanied by a Marquart technique mode with 0.001 Fudge factor; zero-shift (values of the alumina standard were input and fixed); vertical shift — *Sycos*; asymmetry — by divergence with HpS/L (values of the alumina NIST standard were input and fixed); Roughness — *rough1* by Pitschke, Hermann, and Matter approach. The structure refinement parameters were as follows: initial atomic positions of Al, Ti, P, and O were set in accordance with Ref.³; Al and Ti shared a joint position; Li positions were fixed); thermal displacement parameters — U, harmonic anisotropic approximation for Al and Ti, isotropic approximation for P, O, and Li (fixed for the latter one on the 0.01 value). Taking into account the XRD limitations related to the low Al concentration, similar Al³⁺ and Ti⁴⁺ electronic density, and low Li⁺ electronic density, we kept the ionic occupancies fixed for all elements. The vertical shift correction *Sycos* was involved in the general refinement to take the sample preparation features into account: the thin layer of powder or a composite membrane sample were placed on the sample holder's flat side with no strict height control provided. The PVdF phase observed in LATP+PVdF samples was not included into refinement as a separate phase and was later assigned due to the peak positions. All refined structures were submitted in The Cambridge Crystallographic Data Centre (CCDC) database in .cif form and can be found in Fig. S7-S9, Section S3.

Membranes Fabrication



Fig. S1. Fabrication routine for LATP+PVdF composite membranes.

Membranes' Permeability

The two-compartment custom-made diffusion cell (Fig. S2) was equipped with the working Pt electrode (1.6-mm diameter), 3-mm glassy-carbon counter electrode, and reference electrode composed of a 0.5-mm Ag wire. The half-cell with the immersed electrodes was filled with only supporting electrolyte (SE), while another half-cell contained 0.5 M TEMPO in the same SE. The studied membrane was placed between the compartments with the 0.785 cm² area. For convenience, 1.0 M LiClO₄ in PC was used as SE in all permeability tests. Cyclic voltammetry (CV) measurements were carried out in the 0.0 - 0.8 V vs. Fc/Fc⁺ potential range and 0.05 V s⁻¹ scan rate at RT. The rates of TEMPO diffusion from the right half-cell to the left (permeability coefficients) were calculated based on the growth of anodic peak current in time via the second Fick law adopted to the cylindric cell geometry (Eq. S1):

$$V\frac{dC_l(t)}{dt} = \frac{AP}{L}(C_r(t) - C_l(t))$$
(S1)

where V represents the volume of the SE in the left half-cell; $C_l(t)$ and $C_r(t)$ are the TEMPO concentrations in the left and right half-cells in the particular moment (t), respectively; A and L are the membrane's active area and thickness, respectively.



Fig. S2. Scheme of the diffusion electrochemical cell for TEMPO permeability measurements; CE, RE, and WE are counter, reference, and working electrodes, respectively.

The growth of a peak current (i_p) was recalculated to the concentrations according to the Randles–Sevcik equation at 25 °C (Eq. S2):

$$i_p = 2.69 \cdot 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} C_l \tag{S2}$$

where *n* represents a number of electrons involved in the redox reaction; *A* is electrode area; *D* is the diffusion coefficient; v is the CV scan rate; C_l is the concentration of the analyzed redox active species (TEMPO).

To avoid unnecessary diffusion coefficients determination, we preliminary calibrated the peak current using series of TEMPO solutions with known concentrations. So, Eq. S2 was simplified to S3:

$$i_p = KC_l \tag{S3}$$

where K is the calibration factor, constant at the certain electrolyte, cell configuration and scan rate.

Galvanostatic Cycling

The theoretical capacity (Q_{theor}), experimental charge/discharge capacity ($Q_{charge/discharge}$), state-of-charge (SoC (%)), and coulombic efficiency (CE), of the Li-TEMPO HFB cell were calculated by Eq. S4-S7, respectively:

$$Q_{theor} \left(\frac{Ah}{L}\right) = \frac{nC_i F}{3600} \tag{S4}$$

$$Q_{charge/discharge}\left(\frac{Ah}{L}\right) = \frac{\int I_{charge/discharge}dt}{V}$$
 (S5)

$$SoC(\%) = \frac{Q_{discharge}}{Q_{theor}} \cdot 100\%$$
(S6)

$$CE = \frac{Q_{charge}}{Q_{discharge}} \cdot 100\% \tag{S7}$$

where *n* represents the number of electrons involved in the redox reaction; *C* is the molar concentration of the redox active species; *F* is the Faraday's constant; $I_{charge/discharge}$ is the current in a certain time frame; *V* is the volume of the catholyte in the cathode cell part.

Section S2. Optimization of membranes' permeability (Fig. S3-S4, Table S1-S2)



Fig. S3. Morphology and microstructure of the LATP+PVdF composite membrane from the previous study ⁴: (a) SEM microphotograph collected in the CBS regime; (b) EDX map of the same region for **carbon**; (c) AFM microphotograph. (d) Microstructure of the pure PVdF membrane fabricated following the previous routine.⁴



Fig. S4. Cross-section SEM images of PVdF membranes fabricated with T_{mix} of 25, 50, 90, and 130 °C; $T_{\text{sub}} = 150$ °C; $T_{\text{dry}} = 90$ °C.

Porosity, %					
<u>Set P.2</u> (T_{sub} variation)					
27 ± 7					
10 ± 9					
10 ± 9					
variation)					
25 ± 7					
19 ± 8					
20 ± 8					
25 ± 7					
	Porosity, % variation) 27 ± 7 10 ± 9 10 ± 9 variation) 25 ± 7 19 ± 8 20 ± 8 25 ± 7				

Table S1. Dry-measured porosity of PVdF polymer membrane samples.

The membranes' porosity (ε) was estimated using the dry method via Eq. S8:

$$\varepsilon = \frac{m_{dry}}{\rho SL} \tag{S8}$$

where m_{dry} represents membrane's weight (g), ρ is true density of PVdF (g mL⁻¹), and SL — sample's area (cm²) and thickness (cm), respectively.

Table S2. Permeability coefficients of <u>Sample A-D</u> — composite membranes fabricated after temperature setting in the stage of filler distribution optimization.

Notation	Brief description	Permeability, 10^{-7} cm ² min ⁻¹
Sample A	LATP filler added into DMF-PVdF solution	2.19 ± 0.24
Sample B	PVdF powder added into DMF-LATP suspension	2.27 ± 0.25
Sample C	DMF-LATP suspension added into DMF-PVdF solution	2.59 ± 0.29
Sample D	PVdF powder added into <i>ultrasonicated</i> DMF- LATP suspension	0.86 ± 0.09



Section S3. Li-TEMPO cell prototyping and testing (Fig. S5-S11; Table S3-S8)

Fig. S5. Cycling performance of Li-TEMPO HFB cell operating with (a) 1.0 M LiClO₄ in PC, SE **I**, (b) 1.0 M LiClO₄ in EC:DEC (1:1 vol.), SE **II**, and (c) 1.0 M LiTFSI in EC:DEC, SE **III**; (d) Nyquist plots obtained for the HFB cell before and after 100 cycles using SE **III**.

Catholyte redox species Concentration	Supporting electrolyte	Initial capacity, Ah L ⁻¹	Capacity retention, % / N cycles	Coulombic efficiency, % / Current, mA cm ⁻²	Membrane	Anode design	Limitations	Ref.
2,2,6,6-Tetra- methylpiperidine-1- oxyl (TEMPO) / 1 mM	0.75 M LiTFSI in ethylene carbonate + diethyl carbonate (EC:DEC 1:1 vol.)	0.025	68 / 50 50 / 100	94 / 0.2	Composite: LATP+PVdF	Direct stack of Li and membrane; several SE drops in-between	Low TEMPO initial availability; high cell resistance	This work
1-Methoxymethyl ferrocene / 100 mM	1 M LiTFSI in 1,2- dimethoxyethane (DME)	-	30 / 100	91 / 20	Porous: Daramic	Graphite felt layer between Li and membrane	DME volatizes in 100 cycles	5
1,4,5,8-Tetraamino- anthraquinone (Disperse Blue-1) / 80 mM	1 M LiTFSI in dimethyl sulfoxide (DMSO)	8	100 / 50	99 / 20	Ion-exchange: Nafion 115	_	Low solubility and affordability of active species	6
TEMPO / 50 mM	1 M LiPF ₆ in propylene carbonate (PC)	0.9	70 / 50	97 / 5	Porous: Celgard	Graphite felt layer between Li and membrane; static TEMPO electrolyte in anode part	TEMPO degradation during cycling	7

Table S3. Comparison of the reported Li-hybrid flow cells in terms of their electrochemical performance and design architecture.

10-Methyl- phenothiazine (MPT) / 50 mM	1 M LiPF ₆ in EC:DEC (1:1 vol.)	1	95 / 1000	99 / 0.2	Ceramic: LAGP	Soaked in SE Celgard layer between Li and membrane	Low catholyte volume – 4 mL	8
MeO-TEMPO	MeO-TEMPO- LiTFSI (1:1) + 17 wt.% H ₂ O ionic liquid	55	84 / 20	- / 0.2	Ceramic: LIC- GC (Li ion- conducting glass ceramic	Several SE drops on Li surface	Low catholyte volume – 50 µL	9
TEMPO / 100 mM	1.0 M LiPF ₆ in EC:PC:EMC (4:1:5) + 15 wt.% FEC	2.5	99 / 100	99 / 5	Porous: polyethylene- based	Electrically stacked Li and graphite felt; static TEMPO electrolyte in anode part	Highly corrosive LiPF ₆	10
Anthraquinone-based / 250 mM	1 M LiPF ₆ in PC	0.11	70 / 40	93 / 0.1	Porous: Celgard	_	Low cell voltage	11
1,4-Benzoquinone / 10 mM	1 M LiClO4 in γ- butyrolactone (GBL)	0.5 Ah g ⁻ 1	77 / 25 50 / 100	- / 0.05	Ceramic: LIC- GC	Glass filter between Li and membrane	Fast capacity decay	12



Fig. S7. The experimental, refined, and differential XRD patterns of the LATP ceramics sample, as well as R-factors, calculated cell (a, c, V) parameters, and intrastructural polyhedra volumes $([MO_6], [Li(1)O_6M_2])$. CCDC deposition number: 2243668.

Positi on	a_i	x	у	Z.	$U_{ m iso}$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	0.15	0	0	0.14156(4)	0.0122(3)	0.0130(4)	0.0130(4)	0.0105(6)	0.0065(2)	0	0
Ti	0.85	0	0	0.14156(4)	0.0122(3)	0.0130(4)	0.0130(4)	0.0105(6)	0.0065(2)	0	0
Р	1	0.2886(1)	0	0.25	0.0169(3)						
01	1	0.1817(2)	0.9915(2)	0.19000(6)	0.0142(5)						
O2	1	0.1861(2)	0.1630(1)	0.0822(1)	0.0089(5)						
Lil	1	0	0	0	0.01						
Li2	0.05	0.073	0.34	0.091	0.01						

Li2

Table S4. Atomic positions, occupancies (a_i) , coordinates (x, y, z), and thermal displacement parameters (U_{iso} , U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23}) for the LATP ceramic sample.



Fig. S8. The experimental, refined, and differential PXRD patterns of the LATP+PVdF membrane sample *before* cycling, as well as R-factors, calculated cell parameters (a, c, V), and intrastructural polyhedra volumes ([MO₆], [Li(1)O₆M₂]). The α -PVdF phase peak positions correspond to those described in Ref.¹³ CCDC deposition number: 2243666.

Table S5. Atomic positions, occupancies (a_i), coordinates (x, y, z), and thermal displacement parameters (U_{iso} , U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23}) for the **LATP+PVdF membrane** sample *before* cycling

Position	a_i	x	у	z	$U_{ m iso}$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	0.15	0	0	0.1417(3)	0.041(3)	0.040(3)	0.040(3)	0.044(7)	0.020(1)	0	0
Ti	0.85	0	0	0.1417(3)	0.041(3)	0.040(3)	0.040(3)	0.044(7)	0.020(1)	0	0
Р	1	0.2921(8)	0	0.25	0.050(3)						
O2	1	0.189(1)	0.1653(8)	0.0838(9)	0.040(4)						
01	1	0.183(1)	0.9812(9)	0.1888(4)	0.032(3)						
Li1	1	0	0	0	0.01						
Li2	0.05	0.073	0.34	0.091	0.01						



Fig. S9. The experimental, refined, and differential PXRD patterns of the LATP+PVdF membrane sample *after* cycling, as well as R-factors, calculated cell parameters (a, c, V), and intrastructural polyhedra volumes ([MO₆], [Li(1)O₆M₂]). The α -PVdF phase peak positions correspond to those described in Ref.¹³ CCDC deposition number: 2243667.

Table S6. Atomic positions, occupancies (a_i), coordinates (x, y, z), and thermal displacement parameters (U_{iso} , U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23}) for the **LATP+PVdF membrane** sample *after* cycling

Position	a_i	x	у	z	$U_{ m iso}$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	0.15	0	0	0.14126(7)	0.0242(9)	0.0264(9)	0.0264(9)	0.020(2)	0.0132(4)	0	0
Ti	0.85	0	0	0.14126(7)	0.0242(9)	0.0264(9)	0.0264(9)	0.020(2)	0.0132(4)	0	0
Р	1	0.2888(2)	0	0.25	0.031(1)						
01	1	0.1829(3)	0.9893(3)	0.1885(1)	0.029(1)						
O2	1	0.1846(3)	0.1636(3)	0.0813(2)	0.020(1)						
Li1	1	0	0	0	0.01						
Li2	0.05	0.073	0.34	0.091	0.01						



Fig. S10. TEM-EDX images of LATP ceramic particles blended in a PVdF matrix within the LATP+PVdF composite membrane before (pristine) and after 100 charge/discharge cycles in Li-TEMPO HFB cell.



Fig. S11. FTIR spectra of the LATP+PVdF membrane after 100 charge/discharge cycles in Li-TEMPO HFB cell.

Table S7. Summary of the composite membrane fabrication conditions varied within the current and our previous studies devoted to the LATP+PVdF development.

Fabrication parameter	Variation range	Optimized parameter's value	Figure of merit / Final characteristic	Ref.
Polymer PVdF membrane				
Solvent:polymer (DMF:PVdF) ratio	8-20 wt.% PVdF in DMF	15 wt.% PVdF	Thickness / 15-20 μm	14
Pretreatment of the casting glass substrate	A set of washing and treatment approaches	Washing with acetone \rightarrow drying in air flow \rightarrow treatment in plasma	Contact angle between substrate and water / ~1 $^{\circ}$	14
Components mixing temperature (T_{mix})	25–130 °C	25 °C	CV-based evaluation (permeability tests), SEM, FTIR, Raman / diminished globularity and permeability	This work
Solution casting (substrate) temperature (T_{sub})	70–150 °C	150 °C	SEM, Raman, dry porosity, permeability tests / diminished globularity and permeability	This work
Sample drying temperature (T_{dry})	25–130 °C	90 °C	SEM, dry porosity / mediate porosity	This work
Drying atmosphere	Temperature (<i>T</i>) + dynamic vacuum (<i>vac</i>); <i>only T</i> ; <i>only vac</i>	Only T	SEM / smooth, solid, and continuous surface	14
LATP ceramic filler				
Preliminary milling time in a high-energy shaker	0–120 min	90 min	Laser particle size analyzer; SEM / ~1 μm mean particle size	4

LATP+PVdF composite membrane

Presence of a supporting lithium salt (LiClO ₄) in the matrix	With (7.5 wt.%)/without salt: LATP+LiClO4+PVdF, LATP+PVdF	LATP+PVdF	Weight change after static soaking of the membrane in non-aqueous electrolytes / ~0%	14
Ceramic:polymer (LATP:PVdF) ratio	0-60 wt.% LATP in composite	45 wt.%	EIS, permeability tests / trade-off between IC and permeability: $3.4 \cdot 10^{-4} \text{ S cm}^{-1}$ and $6.6 \cdot 10^{-7} \text{ cm}^2 \text{ min}^{-1}$	4
Solvent for polymer dissolution	DMF, DMSO, NMP	All	XRD, FTIR, EIS, permeability tests / close outcomes: IC of $1.0-1.7 \cdot 10^{-4}$ S cm ⁻¹ , permeability of $2.7-3.1 \cdot 10^{-7}$ cm ² min ⁻¹	15
Ceramic filler distribution	A set of mixing approaches; addition of DMF-LATP suspension sonication step	DMF-LATP sonication \rightarrow adding PVdF \rightarrow mixing	Permeability tests, SEM / IC and permeability of <u>final composite</u> : $1.1 \cdot 10^{-4}$ S cm ⁻¹ and $0.86 \cdot 10^{-7}$ cm ² min ⁻¹	This work
Other minor variations	Casting blade speed, solution degassing conditions	15 mm s ⁻¹ , 20 h at 25 °C	Visual membrane's uniformity, optimized fabrication time	14

Table S8. Dependence of Li-TEMPO HFB's initial discharge capacity (normalized to theoretical) on TEMPO concentration in the catholyte during first cycles. Catholyte volume (~12 mL) and supporting electrolyte composition (LiTFSI+EC:DEC) are constant.

Concentration, mM	Initial capacity, %
1	93
10	12
100	~1

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