Cost-effective non-fluorinated composite membranes for vanadium redox flow batteries: a scalable approach for long-duration energy storage

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1. Introduction

Vanadium redox flow batteries (VRFBs) are among the most technically robust options for multi-hour, grid-scale energy storage. The architecture decouples power and energy ratings, uses a single active element in both half-cells, and relies on a non-flammable aqueous electrolyte that removes thermal-runaway risk.

The membrane is the key cost and performance bottleneck. Perfluorosulfonic acid (PFSA/Nafion) membranes account for **≈37 % of stack CAPEX** at USD 500–1,000 m^{-2}, against an industry target of USD 50 m^{-2}. Two compounding pressures reinforce the case for non-fluorinated alternatives:

Vanadium Crossover
PFSA membranes suffer significant V-ion crossover, causing capacity fade and efficiency loss over multi-year deployment.

PFAS Regulation
ECHA REACH restriction on PFAS updated August 2025; adoption expected 2026–27. Critical risk for 15–20 year VRFB deployments.

2. Non-Fluorinated Chemistry Families

Sulfonated hydrocarbons (SPEEK / SPAEK)

Most extensively studied alternative. Precursor cost ~10× below PFSA. SPEEK/COF composites achieve CE 99.8 % at 80 mA cm^{-2} with VO^{2+} permeability 4.02 × 10^{-9} cm^2 s^{-1}; SPEEK/ZrO_2 hybrids reach proton conductivity 0.24 S cm^{-1} and EE > 81 % at 200 mA cm^{-2}. Key unresolved issue: oxidative desulfonation above 50 °C under sustained VO_2^+ exposure.

EE > 81 %
200 mA cm^{-2}

Polybenzimidazole (PBI)

Free mineral acid retained by acid–base interaction with imidazole nitrogen — not covalently bound sulfonates — removing the dominant oxidative-degradation pathway. V-ion permeability one to two orders of magnitude below PFSA. Porous PBI/SiO_2 (40 wt%): CE 99.5–100 %, EE 87.9 % at 80 mA cm^{-2}. Recent commercial benchmarks: ~USD 180 m^{-2}, with 35 % cost reduction 2023–25.

EE 87.9 %
80 mA cm^{-2}

Anion-exchange membranes (AEMs)

Positively charged matrix excludes vanadium cations via Donnan repulsion. CE ≈ 100 % over 100 cycles at 50–80 mA cm^{-2}. PPO/PBI-OO/sulfonated PES blend: stable over 550 cycles at 40 mA cm^{-2} with no detectable capacity decay. Open concern: quaternary ammonium oxidative degradation documented after 30 days of VO_2^+ exposure at 40 °C.

550 cycles
no capacity decay

Porous separators

Size and charge exclusion through engineered pore architectures. Surface-modified PEI membranes with sub-nanometre pores (4.0–8.2 Å) sieve hydrated vanadium ions whilst preserving rapid proton transport. Cost floor ~USD 10 m^{-2} at 100,000 m^2 yr^{-1}. Long-term durability under cycling — pore compaction, fouling, edge erosion — remains an open question.

~USD 10 m^{-2}
cost floor

3. Proposed PBI–SiO_2 Composite Membrane

3.1 Design rationale

The proposed membrane combines a polybenzimidazole (PBI) matrix with inorganic silica as a structural and functional filler. PBI provides the most favourable combination of chemical stability and ultra-low vanadium permeability; silica provides mechanical reinforcement, enhances acid retention through its hydrophilic surface, and generates controlled porosity. The composite inherits the strengths of both components whilst addressing their individual weaknesses: mechanical fragility at high acid doping (pristine PBI) and lack of intrinsic ion-selective transport (pristine silica).

3.2 Synthesis — sol-gel route

TEOS in PBI/DMAc 20–40 wt% SiO_2 → Acid-catalysed hydrolysis + condensation → Thermal curing 80–120 °C tunnel oven → H_3PO_4 doping 75–85 wt% immersion bath

Two architectural variants: (i) homogeneous composite with uniform SiO_2 distribution, optimised for ease of manufacture; (ii) asymmetric composite with SiO_2 loading graded from high concentration at the catholyte-facing surface to low at the anolyte face, eliminating the delamination risk of bilayer architectures.

3.3 Fabricated membrane samples (laboratory)

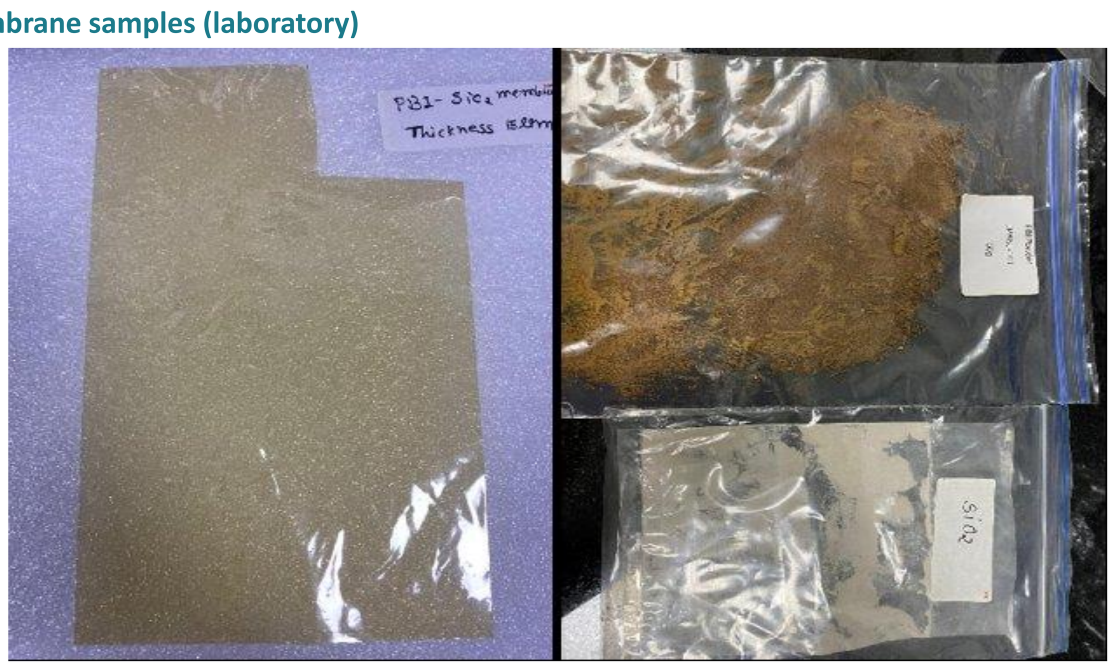

Fig. 1. Laboratory photographs of fabricated PBI–SiO_2 composite membrane samples. Left: cast membrane sheet (label indicates thickness 15 µm). Right: powder and fragment samples at different processing stages.

3.4 Membrane cross-section schematic

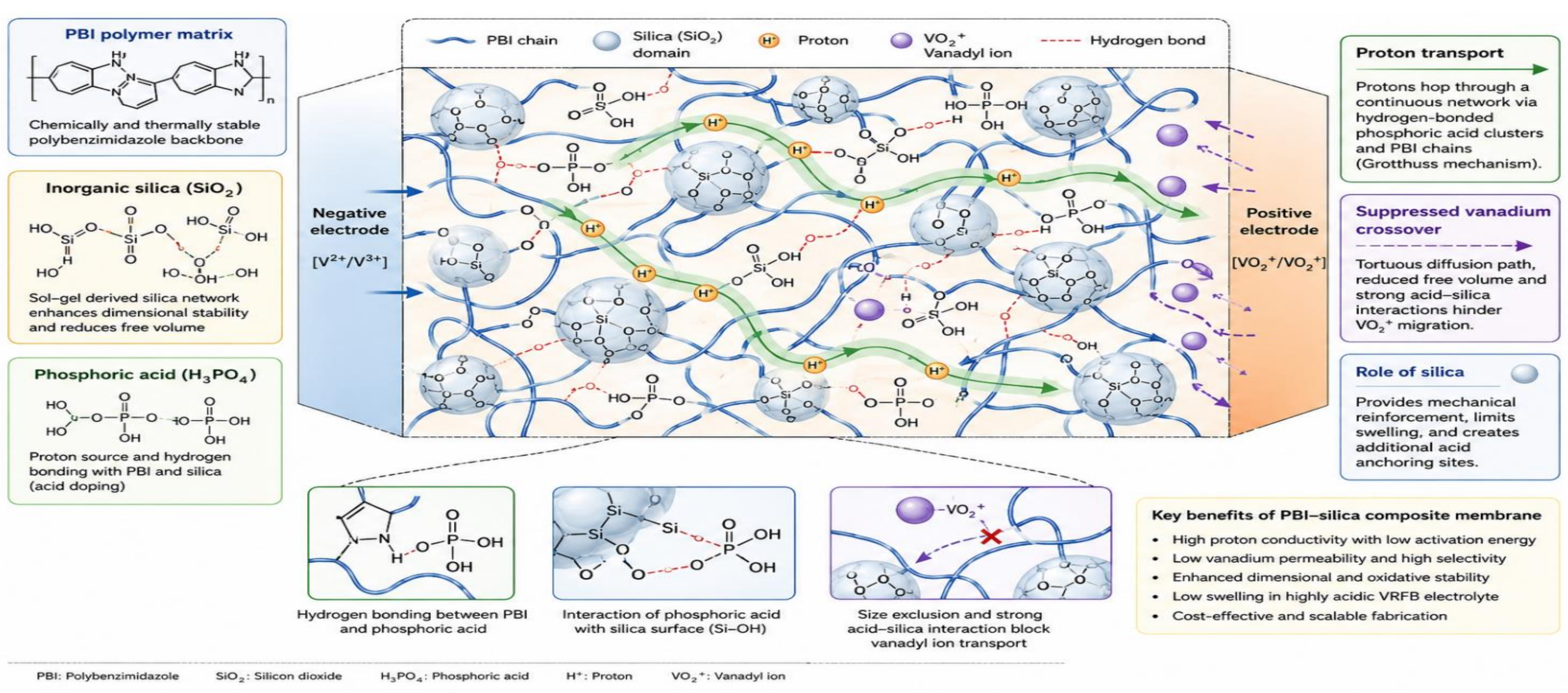

Fig. 2. Schematic illustration of the phosphoric-acid-doped PBI-silica composite membrane showing proton transport pathways, silica-assisted acid retention, and suppression of vanadium-ion crossover in vanadium redox flow batteries (VRFBs)

Keywords: vanadium redox flow battery · non-fluorinated membrane · polybenzimidazole · PBI–silica composite · long-duration energy storage · PFAS

3.5 FTarget Performance Specifications

Parameter	Target value
Thickness	35–50 µm
Silica loading	20–40 wt%
H_3PO_4 doping level	75–85 wt%
Area resistance	≤ 0.6 Ω cm^2
Proton conductivity	≥ 80 mS cm^{-1}
VO_2^+ permeability	< 10^{-9} cm^2 min^{-1}
CE at 100 mA cm^{-2}	**≥ 99 %**
EE at 100 mA cm^{-2}	**≥ 85 %**
Capacity retention	≥ 99.5 % $cycle^{-1}$
Cycling endurance	**> 500 cycles**
Manufacturing cost target	**≤ USD 100 m^{-2}**

Table 1. Target performance specifications for the proposed PBI–SiO_2 composite membrane. Highlighted rows are the primary commercial performance indicators.

4. Characterisation Approach

Physicochemical

- FT-IR: Si–O–Si stretching at 1080, 800 cm^{-1}; imidazole N–H bending
- TGA: thermal stability and quantitative acid retention
- SEM/EDX: silica distribution; gradient verification for asymmetric variant
- Water uptake and swelling in 1.5 M $VOSO_4$ / 2 M H_2SO_4 at 25 and 50 °C
- Tensile properties per ASTM D882

Single-cell electrochemical performance

- 25 cm^2 VRFB cell; graphite-felt electrodes; serpentine flow fields
- 1.5 M $VOSO_4$ / 2 M H_2SO_4 at 50 mL min^{-1}
- 40–200 mA cm^{-2}; cut-offs 1.65 V charge / 0.8 V discharge
- CE, VE, EE over ≥ 500 cycles at 100 mA cm^{-2}
- EPDM and Viton gaskets: 30-day soak in 4 M H_2SO_4 at 50 °C

Ion-transport behaviour

- AC-EIS proton conductivity, four-probe in-plane, 25–60 °C
- VO^{2+} permeability by static H-cell; UV-Vis tracking at 765 nm
- Selectivity figure of merit vs. Nafion 117
- Higher SiO_2 loading reduces V permeability via tortuosity with smaller impact on proton conductivity

Accelerated chemical stability

- Immersion in 0.1 M VO_2^+ / 3 M H_2SO_4 at 40 °C
- ICP-OES: dissolved nitrogen as indicator of imidazole-ring degradation
- Conductivity and mechanical strength tracked monthly, 6-month window
- Free-acid doping expected to eliminate dominant SPEEK oxidative pathway

5. Manufacturing & Cost Considerations

5.1 Scalable fabrication

The sol-gel pre-mix uses standard acid-catalysis reactors. The casting solution is rheologically compatible with both batch solvent casting and continuous roll-to-roll processing on solvent-handling lines used for polyimide and aramid film production.

DMAc solvent recovery through standard distillation is well established at industrial scale. Thermal curing uses tunnel ovens at 80–120 °C; acid doping is achieved by immersion in temperature-controlled H_3PO_4 baths — both standard unit operations in PBI manufacturing.

Both the PBI feedstock and TEOS silica precursor are available from Indian and Asia-Pacific suppliers. DMAc and curing equipment can be qualified through Indian fabrication houses serving the polyimide film and lithium-cell separator markets.

5.2 Cost benchmark

Category	USD m^{-2}	Status
Nafion (PFSA)	180	Commercial
SPEEK / SPAEK	70	Pilot
PBI composites	80–180	Lab–early commercial
AEMs	N/R	Laboratory
Porous separators	~10	Lab–pilot
PBI–SiO_2 (this work)	**≤ 100 (target)**	R&D

Table 2. Manufactured-cost estimates at 100,000 m^2 yr^{-1} [4, 19]. Proposed membrane targets PBI performance ceiling at near-SPEEK cost via silica substitution.

6. Conclusions & Outlook

1. PBI-based composites currently offer the most favourable combination of chemical stability, ultra-low vanadium permeability, and cycling endurance among non-fluorinated chemistries.
2. The proposed PBI–SiO_2 composite consolidates the strengths of both components and is engineered for scalable roll-to-roll manufacture.
3. Target envelope: CE ≥ 99 %, EE ≥ 85 % at 100 mA cm^{-2}, > 500 cycles, ≤ USD 100 m^{-2} — within demonstrated PBI-composite capability.
4. PFAS regulatory hardening will accelerate non-fluorinated membranes from a cost-driven preference to a design default for long-duration deployments.

Validation roadmap

Lab characterisation
FT-IR · TGA
SEM · EIS
↓
25 cm^2 single cell
CE, VE, EE
≥ 500 cycles
↓
1 kW short stack
Stack integration
sealing tests
↓
Accelerated ageing
6 months
ICP-OES

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