New-Generation P+ Cation for High-Voltage Redox-Flow Batteries

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Background

Redox-Flow Batteries (RFBs)

- ✓ Reversible fuel cells
- ✓ Decoupled power delivery and energy storage
- ✓ Excellent scalability and durability
- ✓ Low cost compared with other batteries in large scale
- ✓ Easy management of both electrolytes and cells

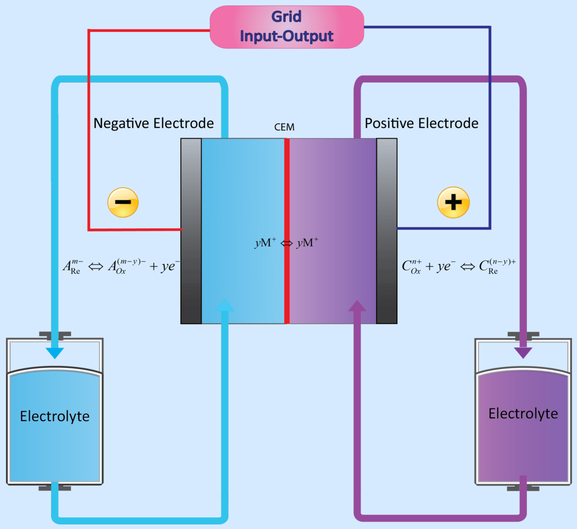

Fig 1. General schematic of redox-flow batteries

Cerium-Based High-Voltage RFBs

Cerium Redox Pair-Based RFBs

- ✓ Very high redox potential (1.74~1.87 V vs. SHE)
- ✓ Very high cell voltage (*e.g.*, Pb-Ce RFB with **1.87 V**; V-Ce RFB with **2.00 V**; Zn (acid)-Ce RFB with **2.50 V;** and Zn (base)-Ce RFB with **3.08 V**)
- ✓ Very facile redox kinetics (~10 mV overpotential at 100 mA/cm^2 on carbon felt electrodes)
- ✓ Good solubility (*e.g.*, 1 mol/L)
- ✓ Potentially high energy density and high power density
- ✓ Low RFB cost

Key Challenge Facing Cerium-Based RFBs

- ✓ Sufficient stability and durability of polymer anion-exchange membranes against highly-oxidative cerium(IV) ions (*e.g.*, Ce^{4+} in sulfuric acid or Ce_2O^{6+} in perchloric acid)

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Two Generations of Phosphonium Cations (Gen 1 and Gen 2)

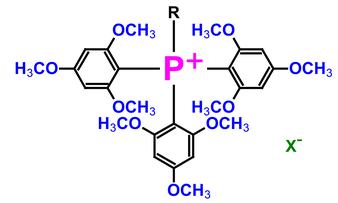
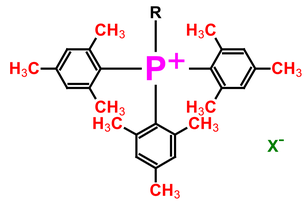
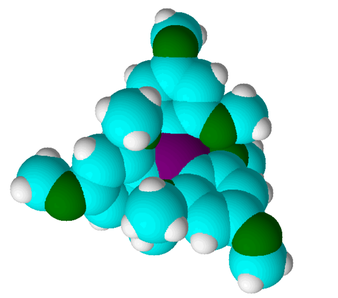
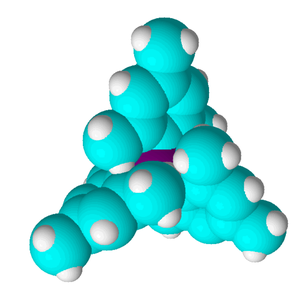
Gen 1 (9MeOs)	Gen 2 (9Mes)
	
	

Fig 2. Structures of the **Gen 1** phosphonium cation (*i.e.*, tris(2,4,6-trimethoxyphenyl) phosphonium, or ***9MeOTTP***$^+$, left column) and the **Gen 2** phosphonium cation (*i.e.*, tris(2,4,6-trimethylphenyl) phosphonium, or ***9MeTTP***$^+$, right column). Chemical structures are on top and spatial structures are on bottom for both **Gen 1** cation and **Gen 2** cation. The key difference between **Gen 1** and **Gen 2** lies in the accessibility to central phosphorus atom (purple ball).

Outstanding Stability (30-Fold Improved)

Our Approach

- ✓ Design of new-generation of phosphonium cation (*i.e.*, tris(2,4,6-trimethylphenyl) phosphonium, or ***9MeTTP***$^+$)
- ✓ Development of new phosphonium cation-functionalized anion-exchange membranes with improved stability

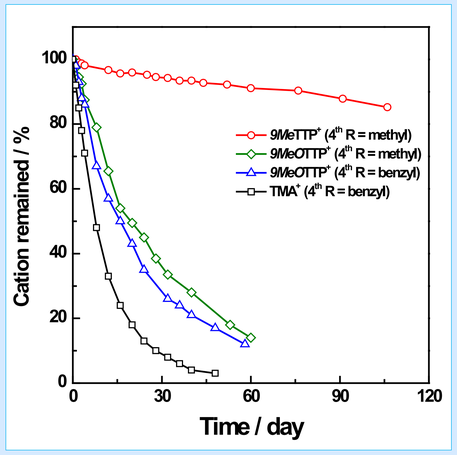


Fig 3. Alkaline stability comparison among the standard trimethyl ammonium cation and the two generations of phosphonium cations. Test conditions and procedure: A 1 M alkaline solution was prepared by dissolving KOD in a 5:1 (vol) mixture of CD_3OD/D_2O. (Note: the purpose of the methanol is to accelerate degradation.) Cation salts were added to the alkaline solution to obtain a molar ratio of 30 KOD : 1 cation (*i.e.*, 0.033 M). A similar quantity of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt ($TMS(CH_2)_3SO_3Na$) was also added to serve as an internal standard. The mixture was held at 80 °C for certain days. ^{31}P NMR spectroscopy was used to determine the degree of degradation for all phosphonium cations, and ^1H NMR spectroscopy for ammonium cation.

Synthetic Strategy

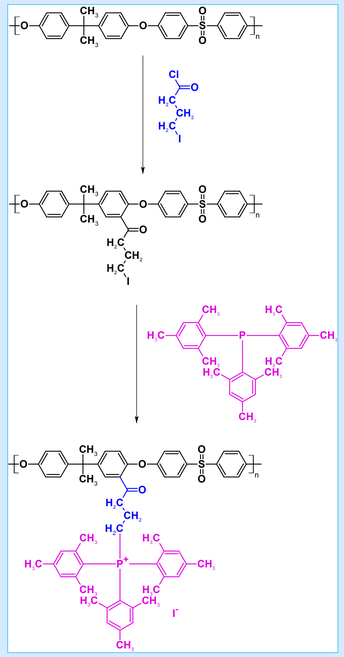


Fig 4. Proposed synthetic strategy for attaching ***9MeTTP***$^+$ cation to polymer backbone. (polysulfone as an example of polymer backbone, and iodoalkylene carbonyl chloride with carbon number = 4 as an example of linkage molecule).

Objective & Impact

Objective

Preparation of a series of highly stable AEMs functionalized with the new-generation phosphonium cation (***9MeTTP***$^+$), tailored for the applications of cerium RFBs and many other alkaline membrane-based durable electrochemical devices such as fuel cells and electrolyzers.

Impact

The development of stable anion-exchange membranes will help make high-voltage RFBs an economically competitive and efficient solution of renewable energy storage.

Acknowledgement

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