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

Cerium-Based High-Voltage 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/cm² 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., Ce⁴⁺ in sulfuric acid or Ce₂O₆⁺ in perchloric acid)

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

Outstanding Stability (30-Fold Improved)

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

Synthetic Strategy

Fig 1. General schematic of redox-flow batteries

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).

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 CO₃OD/D₂O. (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(CH₂)₃SO₃Na) was also added to serve as an internal standard. The mixture was held at 80 °C for certain days. ¹³P NMR spectroscopy was used to determine the degree of degradation for all phosphonium cations, and ¹H NMR spectroscopy for ammonium cation.

Fig 4. Proposed synthetic strategy for attaching 9MeTTP⁺ cation to polymer backbone, (polysulfone as an example of polymer backbone, and polyalkyne carbonyl chloride with carbon number n = 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.

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