

Novel Polyoxovanadate cluster (POV₁₄) for use in Non-aqueous Redox Flow Batteries

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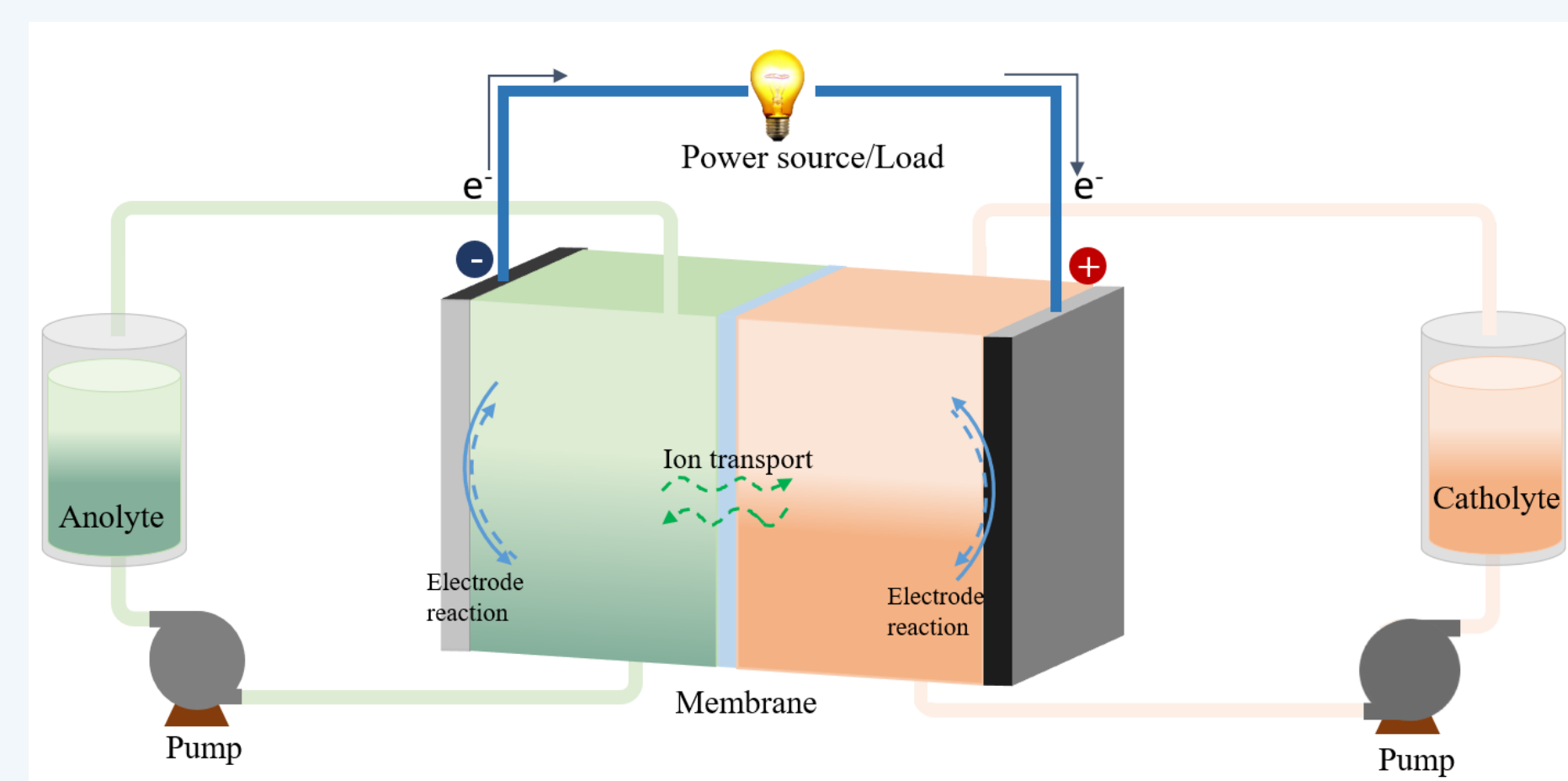
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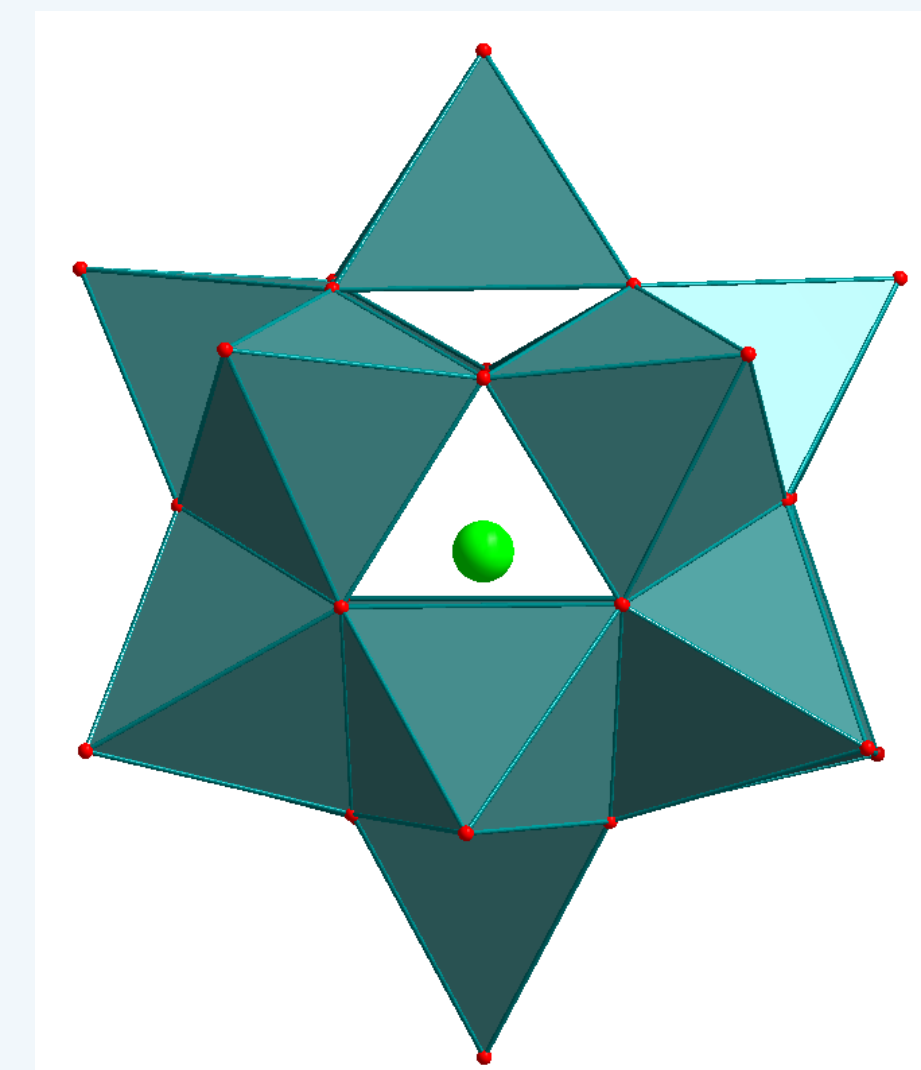
Background and objectives

Schematics of the RFBs



The merits

- Low cost
 - Safe and reliable
 - Flexible and scalable design
- #### The challenges
- Low specific energy density



Structural illustration of TBA₄[V₁₄O₃₄Cl] {POV₁₄}

The advantages of polyoxometalates (POMs) for RFBs

- POMs possess excellent reversible redox-active properties and fast kinetics
- POMs have good chemical and electrochemical stabilities
- POMs can store and transfer multiple electrons per molecule
- POMs' polynuclear structures enable electron delocalization

Redox Flow Batteries (RFBs)

- ◆ The energy is stored and converted via the reversible redox-active species within the electrolyte.
- ◆ The active species in anolyte and catholyte can be different species, dividing into symmetric RFBs and asymmetric RFBs.
- ◆ The battery capacity and power of RFBs are decoupled, making them more suitable for large-scale intermittent energy source.

Our solution

- ◆ Design and synthesize **more soluble POMs** in specific solvent media to improve the energy capacity of RFBs;
- ◆ **Advance the configuration** of RFBs to decrease inner resistance to boost the columbic efficiency of RFBs;
- ◆ Choose the appropriate potential of active species to deliver **multi-electron transfers** per POMs molecule.

Electrochemical properties of POV₁₄

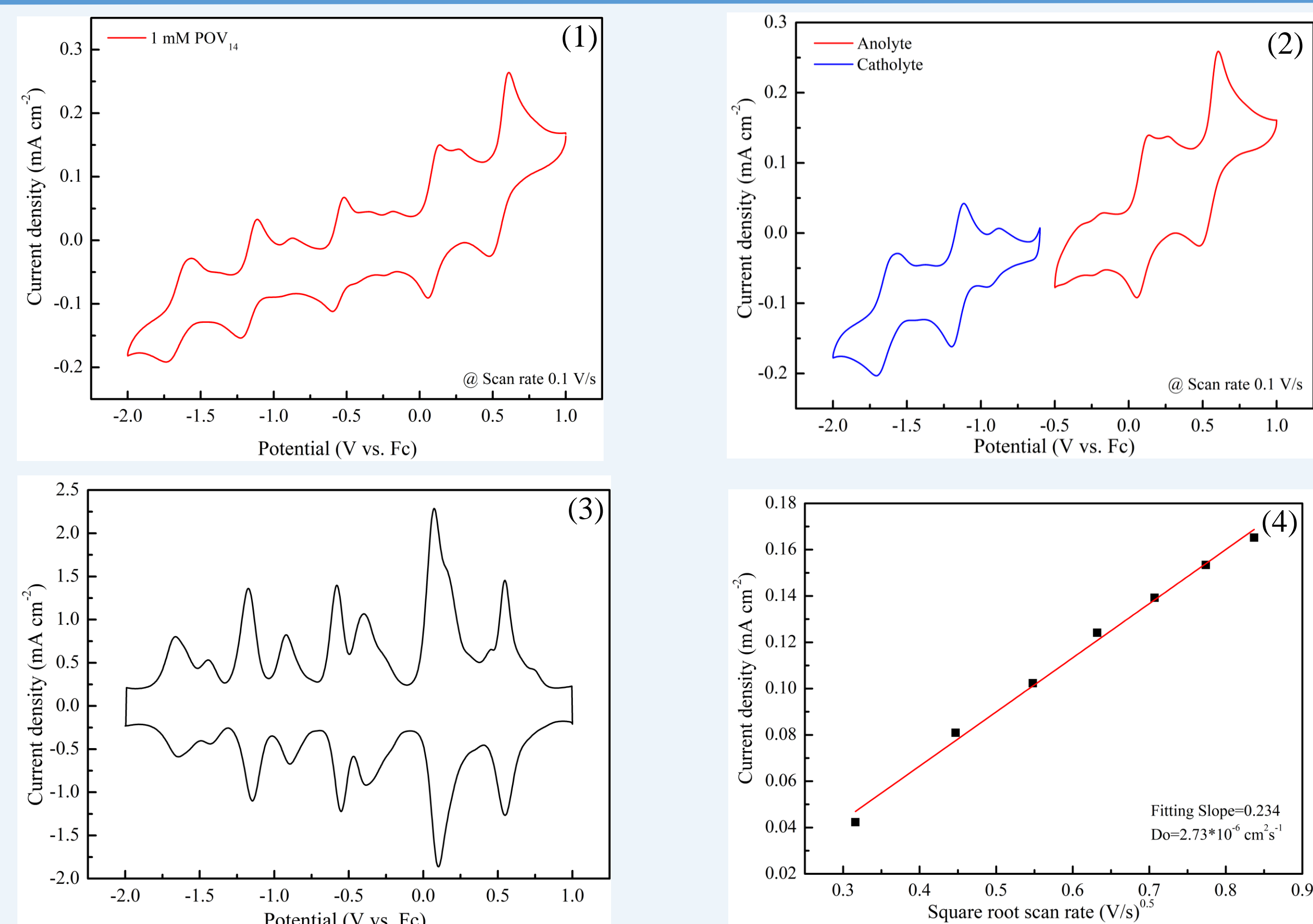


Fig. 1. Electrocatalytic performance of 1 mM POV₁₄ in acetonitrile with 0.1 TBAPF₆ as supporting electrolyte. (1) and (2) CV curves of POV₁₄ at scan rate of 0.1 V/s OER polarization curves of different catalysts, (3) SWV of POV₁₄ at scan rate of 0.1 V/s (4) Diffusion coefficient of POV₁₄ at potential peak at -1.2V.

Characterizations of the RFBs

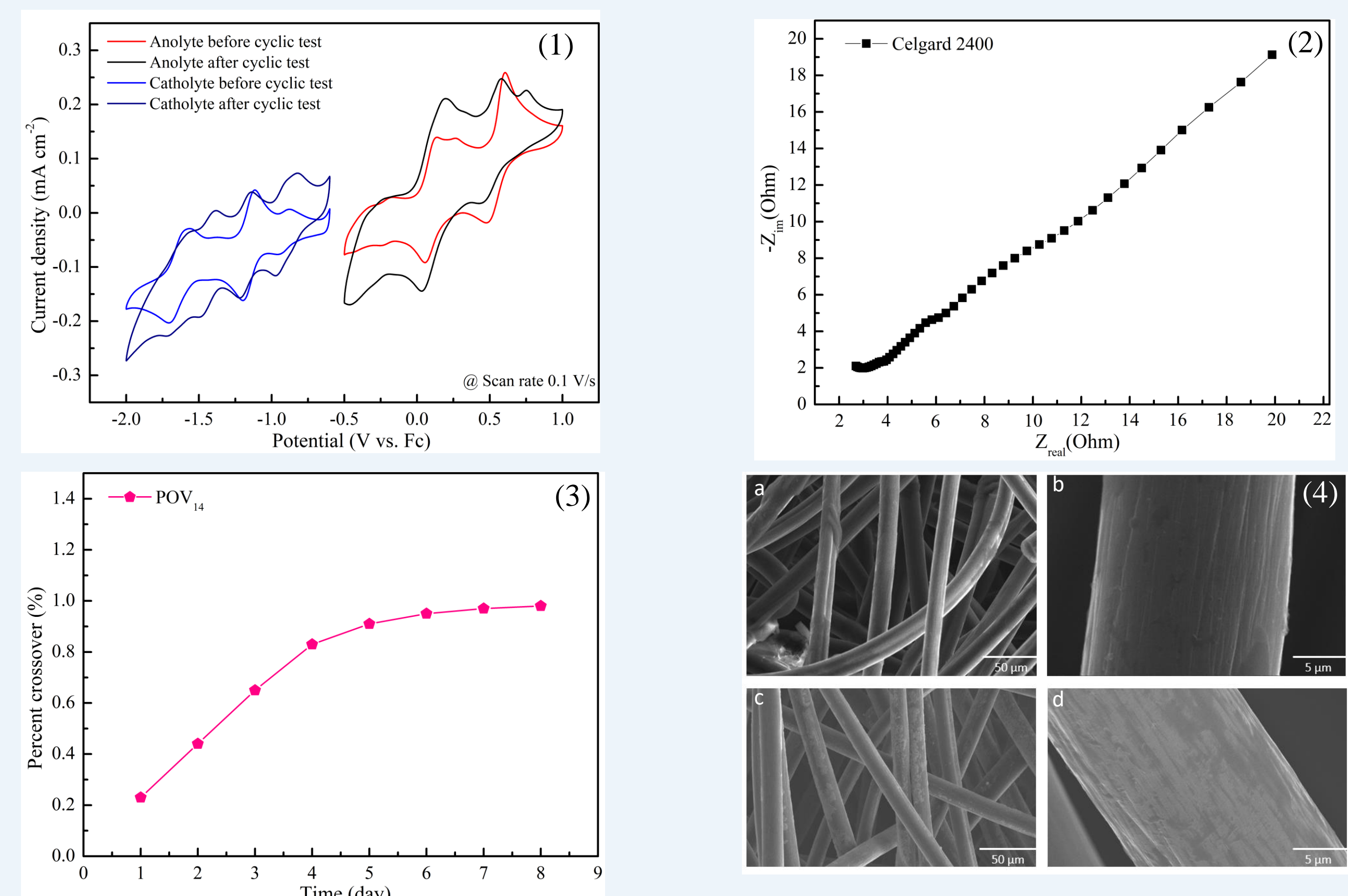


Fig. 3. Characterization of the electrolyte and RFBs properties. (1) CV profiles of the electrolytes before and after the cyclic test at scan rate of 0.1 V s⁻¹. (2) Impedance of the RFBs with modified Celgard 2400 membrane. (3) The percentage of POV₁₄ crossover the Celgard membrane during the static diffusion test. (4) SEM images of the electrodes before (a, b) and after the cyclic test (c, d).

The performances of RFBs

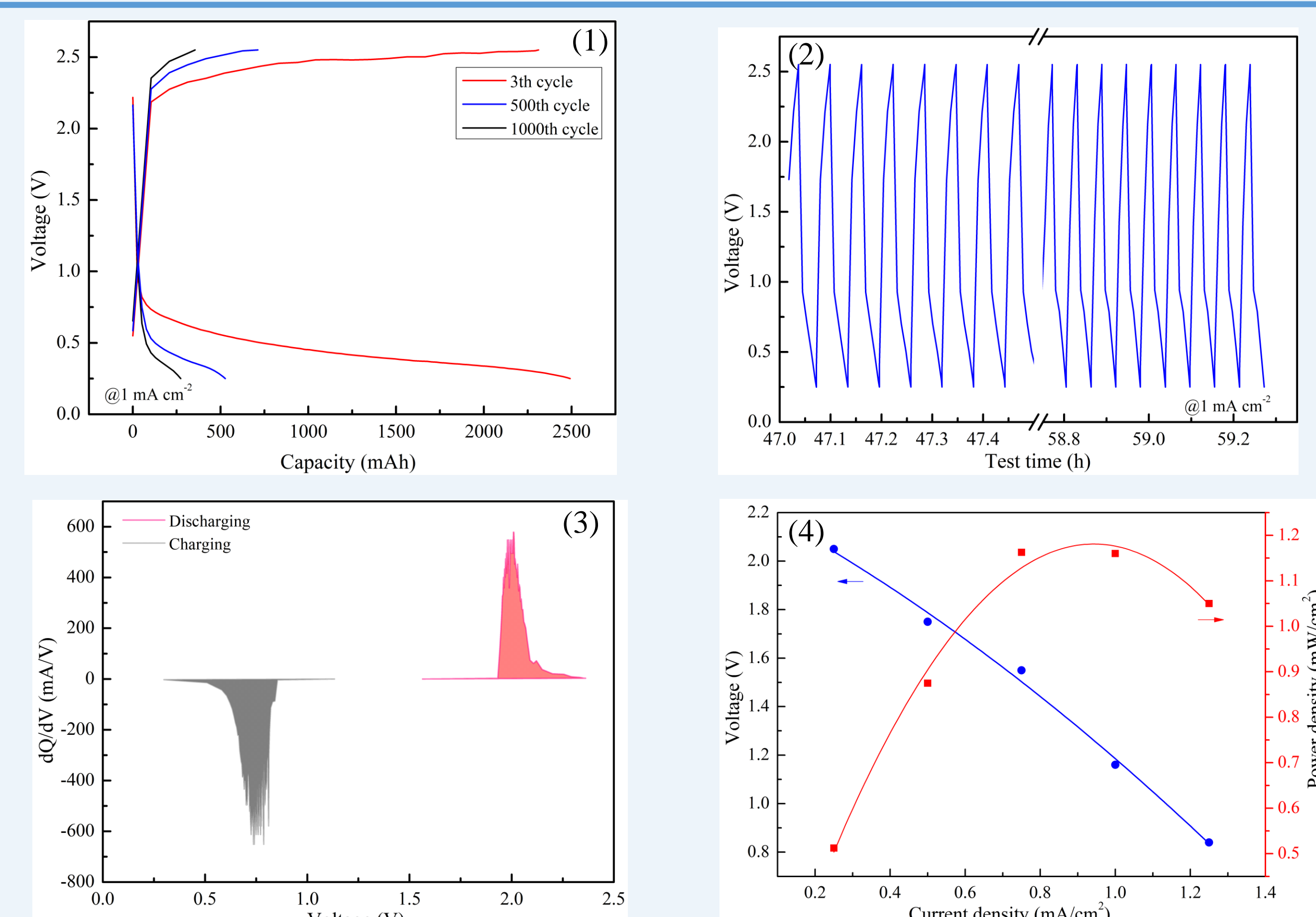


Fig. 2. Performances of the RFBs used 1 mM POV₁₄ as electrolyte with 0.1 M TBAPF₆ as supporting electrolyte. (1) Charging-discharging profiles at current density of 1 mA cm⁻². (2) Voltage curve in cyclability tests at current density of 1 mA cm⁻². (3) The dQ/dV charging-discharging curve at cut-off voltage of 0.25 V and 2.2 V. (4) Battery Polarization curve and power density of the battery at 100% SOC.

Outlook

- ❖ A novel polyoxovanadate cluster TBA₄[V₁₄O₃₄Cl] {POV₁₄} was firstly used for symmetric RFBs, the battery delivered a specific capacity of 2.5 Ah L⁻¹ with stable cyclic performance over 200 cycles.
- ❖ Targeted synthetic strategies for new polyoxometalates clusters, including cation exchange, ligand substitution, heterometal installation, marking a new direction for the application of polyoxometalates in RFBs.
- ❖ Electrodes modification and hybrid solvents for RFBs will be tested in attempt to improve the battery performances.

References

- [1] T. Feng, H. Wang, Y. Xiang, F.-S. Lu, J Power Sources, 436 (2019) 226831–226839.
- [2] J. Friedl, M.V. Cunz, F. Cording, Energy Environ. Sci. 11 (2018) 3010–3018.
- [3] J.-J. Chen, M.D. Symes, L. Cronin, Nat. Chem. 10 (2018) 1042–1047.
- [4] M. Anjass, G. A. Lowe, C. Streb, Angew. Chem. Int. Ed. 60 (2021), 7522 – 7532.

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