Electronic Supporting Information (ESI)

Investigation of Novel Hybrid Europium/TEMPTMA-based Neutral pH Aqueous Redox Flow Batteries

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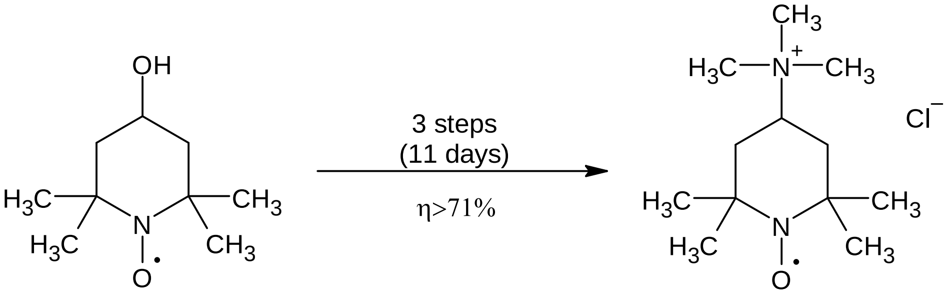
1) Syntheses of used redox-active compounds

Multistep Preparation of TEMPTMA chloride



Step 1: To a 250 mL round bottom flask, ***TEMPOL*** (2,2,6,6-**te**tra**m**ethyl**p**iperidin-1-**o**xyl-4-o**l**, 25 g, 145.14 mmol, 1 eq) was dissolved in 40% DMA in water (120 mL, 1000 mol, 6-7 eq). Afterwards, the reaction mixture was heated up to reflux for 2 days. Then the solvent was evaporated under reduced pressure to give crude of 4-(N,N-dimethylamino)-2,2,6,6-tetramethylpiperidin-1-oxyl as yellowish orange solid. The solid was dried at 50 °C overnight. **Step 2:** Afterwards, the dried crude was dissolved in 200 mL of dry acetonitrile and excess iodomethane (50 mL) was added drop wise. The solution was stirred at 50°C for 3 days under cooling condenser. The iodide salt of 2,2,6,6-tetramethylpiperidin-1-oxyl-4-(N,N,N-trimethylammonium was filtered off via Büchner funnel and the brownish orange solid was dried in air. **Step 3:** Then, the iodide salt was dissolved in 125 mL of distilled water and excess amount of freshly prepared AgCl (30 g, 209-210 mmol) was suspended in this solution. The solution was stirred at room temperature in dark for 5 days to make ion exchange from iodide to chloride with high conversion yield. The solid was filtered off and the water was evaporated under reduced pressure to give pure ***TEMPTMA*** (2,2,6,6-tetramethylpiperidin-1-oxyl-4-(N,N,N-**tri**m**ethyl**a**mmonium) chloride (25.74 g, 103.04 mmol) as pinkish-orange solid. The solid was characterized by EPR spectroscopy and CV techniques.

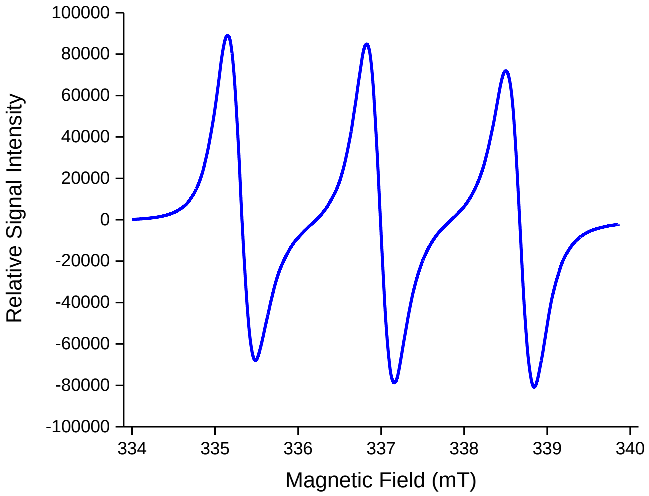
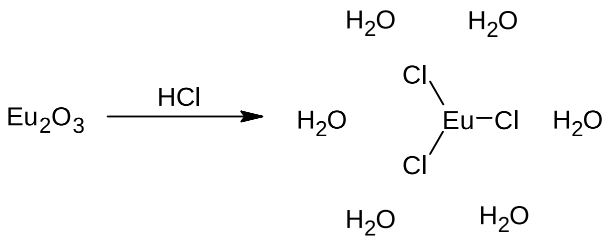


Figure S1 EPR spectrum of TEMPTMA$^+$ in H_2O

Preparation of $EuCl_3.6H_2O$



To a 50 mL round bottom flask, 3.5193 g of Eu_2O_3 (10 mmol, 1 eq) was dissolved in around 20 mL of 3 M HCl (60 mmol, 6 eq) at 50°C. The reaction mixture was stirred at 50°C for 45 minutes. Afterwards, the solvent was evaporated 50°C under reduced pressure to remove excess water and further dried in vacuum oven to give 7.328 g of pure $EuCl_3.6H_2O$ (≃ 20 mmol, 100% conversion). The solid was characterized by CV technique.

2) Electrochemical analyses

Concentration and scan rate dependent experiments were performed using a PalmSens 4 potentiostat with PSTrace software from PalmSens BV (the Netherlands). The experiments were carried out applying 95% of automatic IR drop compensation (Ru values ranging from 15 ohm to 30 ohm) evaluated with the ZIR tool. The glassy carbon disk (d = 3 mm) working electrode was polished with 0.25 µm diamond powder (Büehler) and rinsed with distilled water. Commercial platinum wire and aqueous electrode Ag/AgCl were used as auxiliary and reference electrodes, respectively.

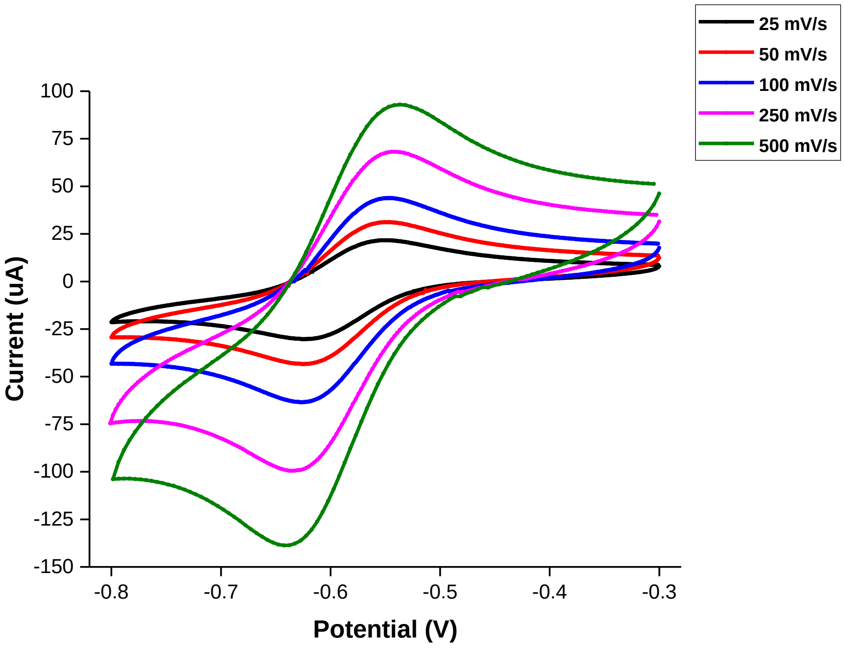


Figure S2 The cyclic voltammogram of mixture of Eu^{3+} (10 mM) in 1 M KCl using glass carbon as working electrode (WE), Pt wire as counter electrode (CE) and Ag/AgCl in 3.5 M KCl as reference electrode (RE) with different scan rates.

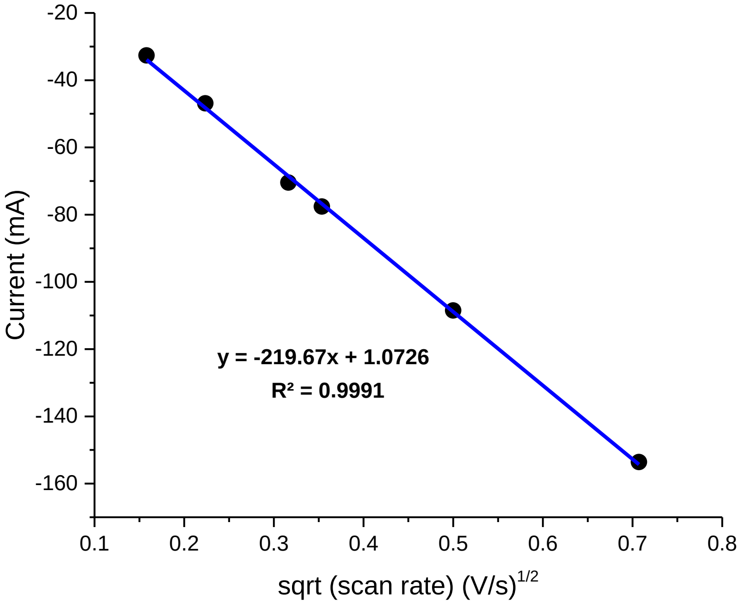


Figure S3 The plot of peak current versus the square root of the scan rate for Eu^{3+} (10 mM) in 1 M KCl

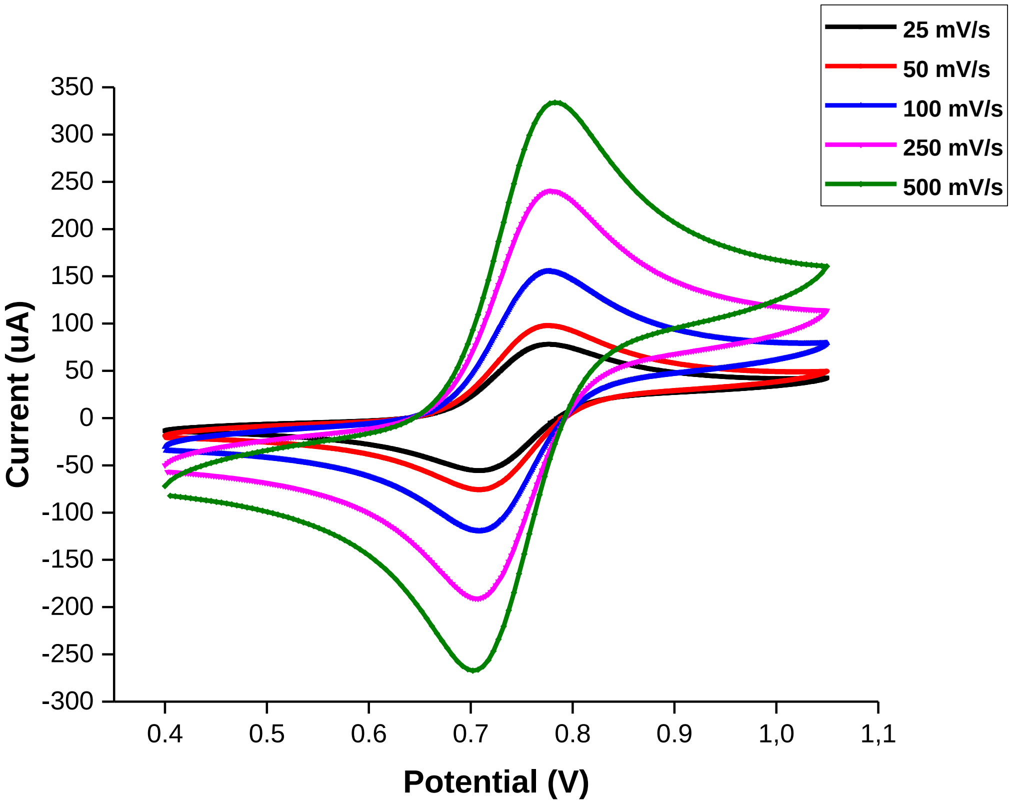


Figure S4 The cyclic voltammogram of mixture of $TEMPTMA^+$ (20 mM) in 1 M KCl using glass carbon as working electrode (WE), Pt wire as counter electrode (CE) and Ag/AgCl in 3.5 M KCl as reference electrode (RE) with different scan rates.

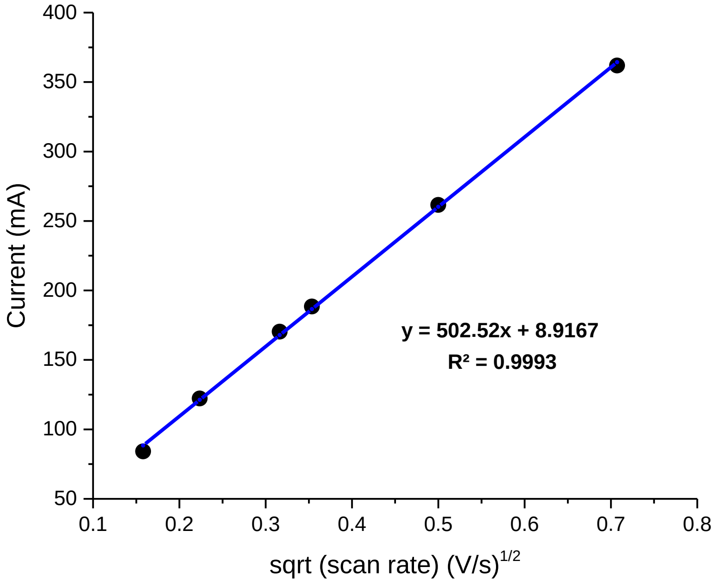


Figure S5 The plot of peak current versus the square root of the scan rate for TEMPTMA$^+$ (20 mM) in 1 M KCl

Diffusion coefficient (D_0)

The diffusion coefficient constants for Eu^{3+} and TEMPTMA$^+$ in 1 M KCl was obtained from cyclic voltammetry data, using the followed Randles-Sevcik equation at reversible process.

$$i_p = 0.4958nFAC_0D_0^{1/2}v^{1/2}\left[\frac{\alpha n_a F}{RT}\right]^{1/2}$$

where *n* is the number of electrons, *F* is Faraday's constant, *A* is the electrode area for 2 mm diameter glassy carbon electrode, C_0 is the bulk concentration of Eu^{3+} (10 mM) and TEMPTMA$^+$ (20 mM) solutions in 1 M KCl, *v* is the scan rate (25, 50, 100, 250 and 500 mV s^{-1}), D_0 is the diffusion coefficient of Eu^{3+} and TEMPTMA$^+$, ɑ is the charge transfer coefficient (0.5), and n_a is the number of electrons involved in the rate-determining step. The slopes of the cathodic and anodic sides, TEMPTMA and Eu^{3+} respectively, are ±0.0001, and the calculated for Eu^{3+}, D_0 is 6.6 $\times 10^{-6}$ cm^2 s^{-1} at 25^{0}C and calculated for TEMPTMA$^+$, D_0 is 9.6 $\times 10^{-6}$ cm^2 s^{-1} at 25^{0}C.

Redox-active specie	**$E_{1/2}$(V vs Ag/AgCl)**	**D_0 (cm^2/s)**
Eu^{3+}	-0.6	$6.6\cdot10^{-6}$
TEMPTMA	+0.75	$9.6\cdot10^{-6}$

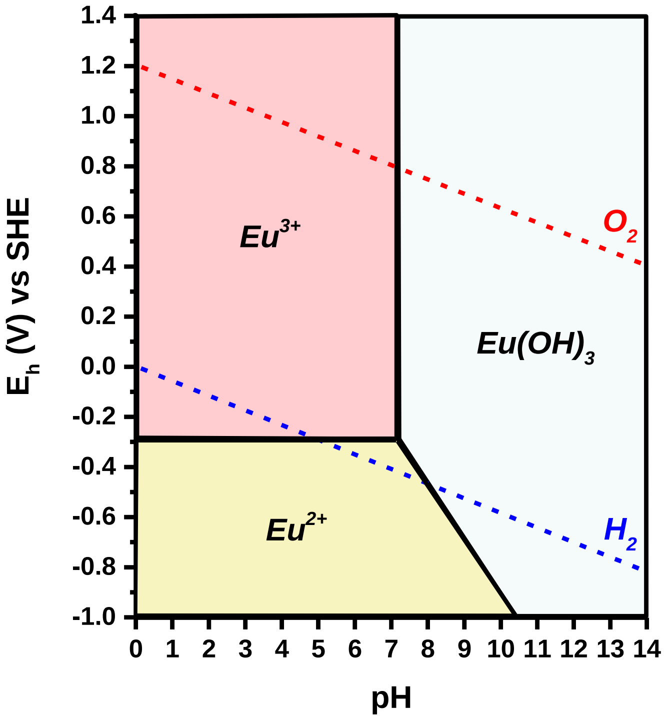
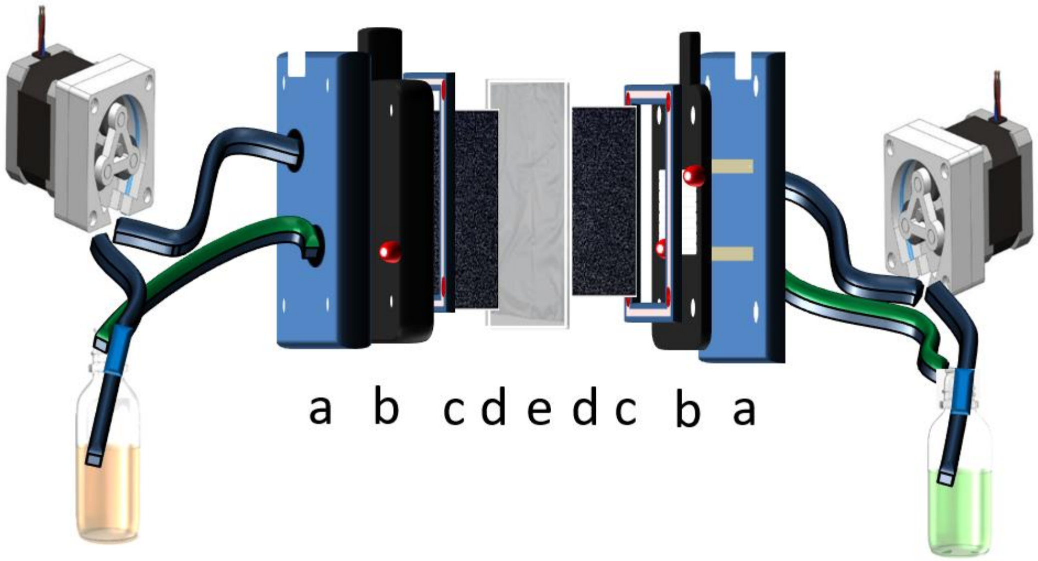


Figure S6 The Pourbaix diagram of relative Eu species depending on potential and pH

3) Battery Tests

To assemble the redox flow battery cell, the tubings are connected between the end plates and tanks using pumps. The components are secured in the correct orientation using plastic sticks placed in the corner holes. A current collector (graphite) plate are placed on one end plate, and a PTFE flow frame is positioned onto the current collector plate to seal the electrolyte flow. The soft electrodes (carbon felt, 2x2.5 cm^2) are inserted into the PTFE frame, ensuring contact with the current collector plate. The electrode are connected to the ion-selective membrane (DSVN – anion exchange membrane) from the opposite side. Finally, install the electrode, flow frame, current collector, and endplate respectively for the other half of the cell. Apply pressure by fastening bolts and nuts for a tight and secure assembly. The liquids were pumped through Masterflex C-Flex tubings (Cole-Parmer, connected to the cell) with a Masterflex L/S, Cole-Parmer peristaltic pump. The flow cells were galvanostatically charged-discharged inside a glovebox using a LANHE Battery Testing System G340A.



Scheme S1 The designed flow battery scheme (a) End-plates (PTFE), (b) Current collectors (Graphite), (c) Gaskets (PTFE), (d) Electrodes (carbon felt), and (e) cation selective exchange membrane (Nafion 212), drawn by Vahid Abbasi

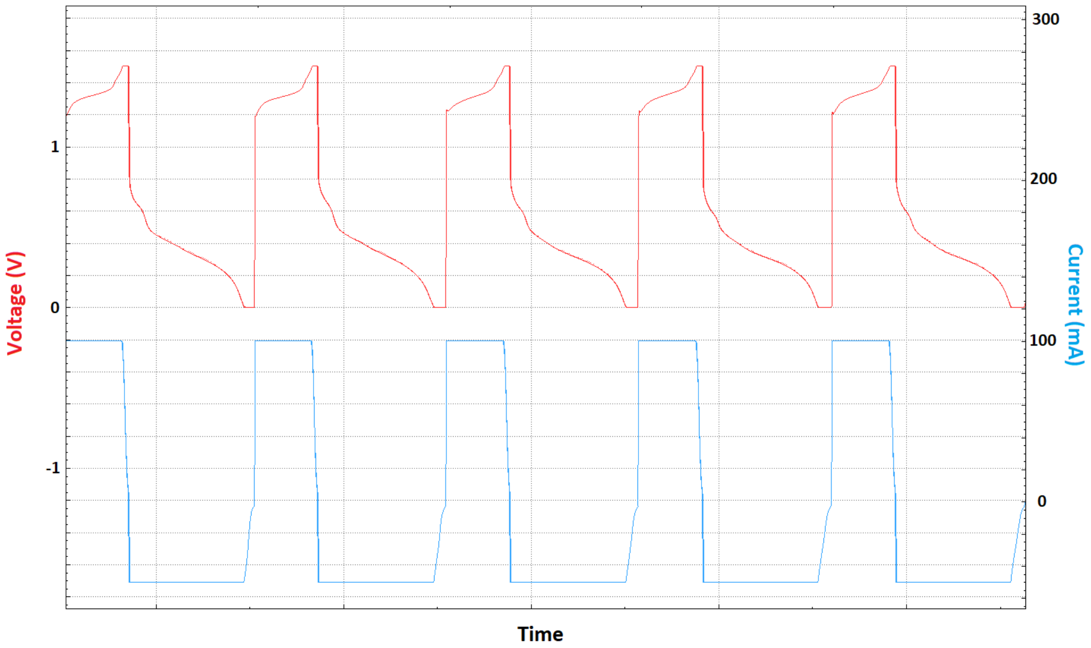


Figure S7 The voltage-current plot of cycling battery system

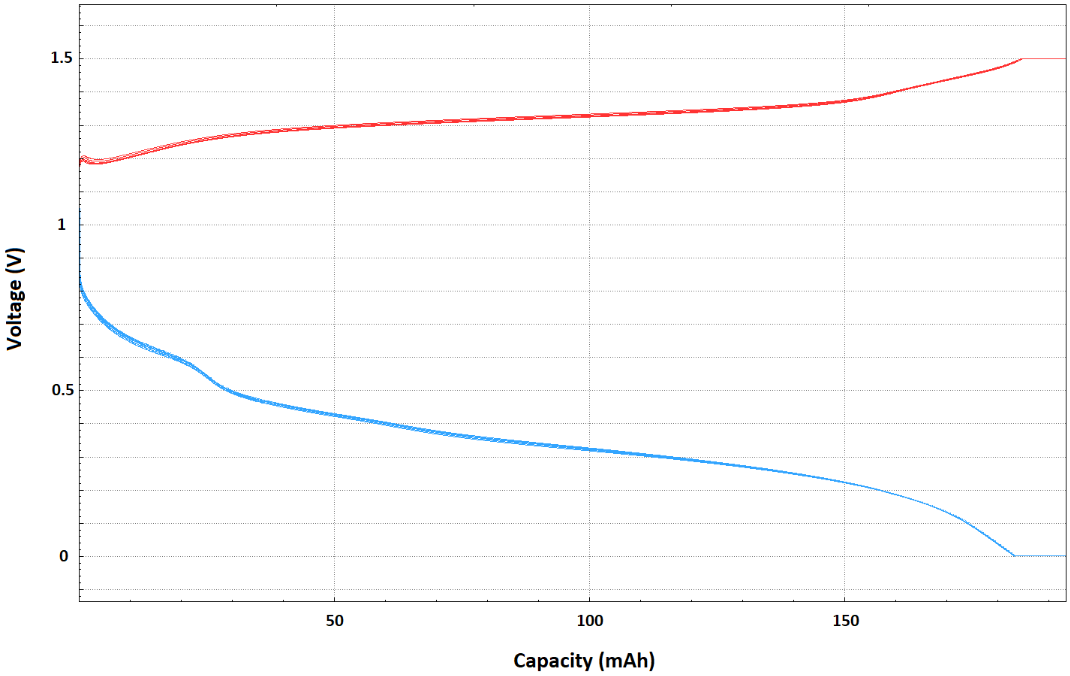


Figure S8 The voltage-discharge capacity plot of cycling battery system

4) Cost Analyses and Capacity Comparisons

Table S1 The battery comparisons for Eu^{3+}-containing systems

Posolyte	Negolyte	pH	V	Cycle Number (Day)	Retention cycle% (per day%)	c (mol/L)	Exp. Disc. Capacity (Ah/L)	Ref.
FcNCl	Eu^{3+}	Neutral	1.02	500 (5.2)	99.88 (96.88)	0.1	~2.7	[16]
Ce^{3+}	Eu^{3+}	Acidic	1.90	10 (~1.4)	96.53 (78.51)	0.5	~1.1	[17]
TEMPTMA	Eu^{3+}	Neutral	1.35	120 (29)	>99.97 (>99.88)	0.25	6.8	This work

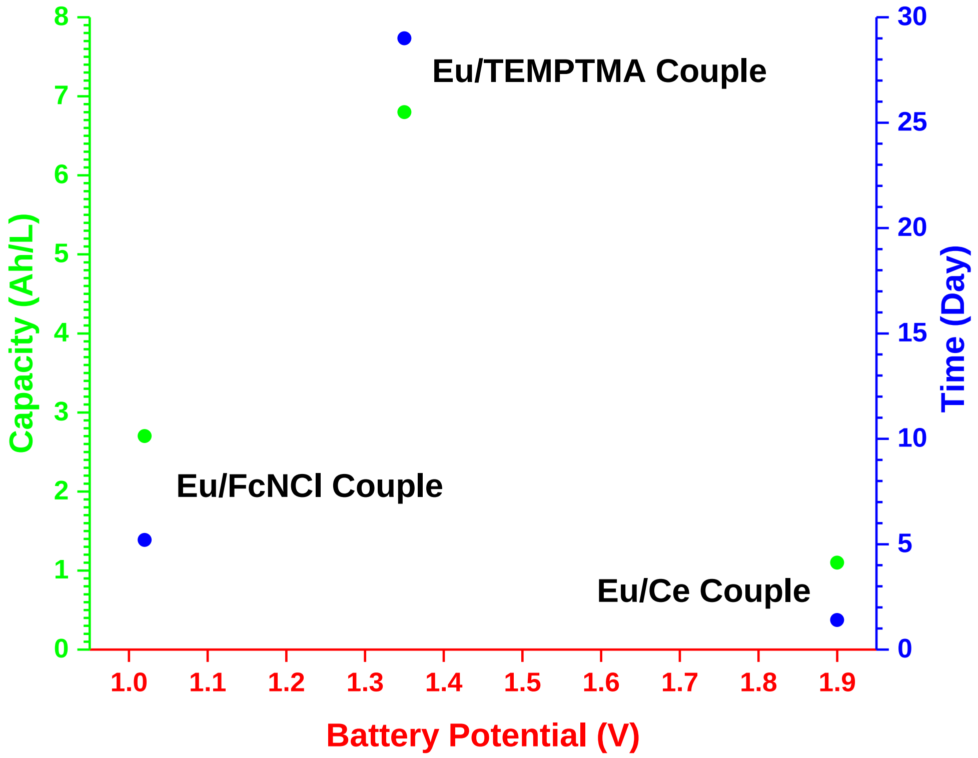


Figure S9 The battery comparisons for Eu^{3+}-containing systems

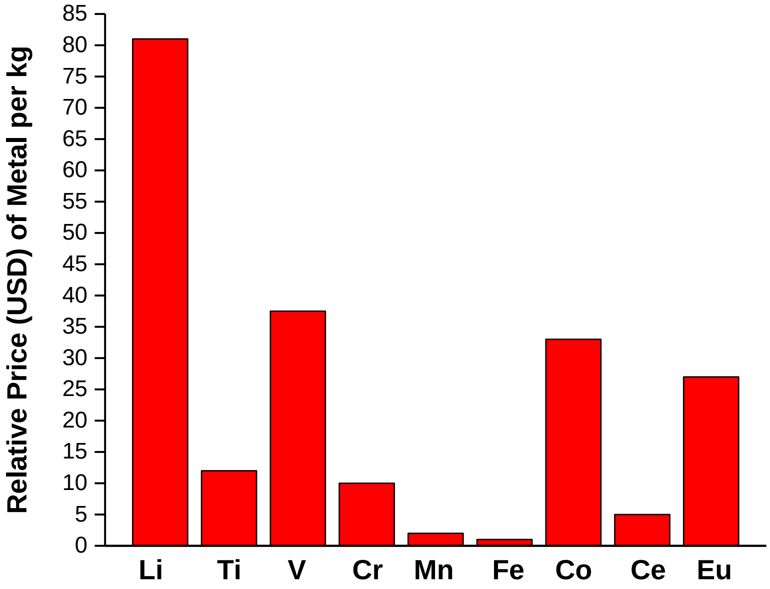


Figure S10 The relative cost analysis for different metals being used in aqueous flow and Li-ion batteries