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

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Abstract: In this study, Eu^{3+}/TEMPTMA-based hybrid aqueous redox flow battery system at 1.35 V in neutral pH containing 1 M KCl media was introduced and this battery system was monitored for a long-term cycling performance. During battery and electrochemical studies, capacity change, self-discharge rate and coulombic efficiencies are examined and diffusion constant (D_0) values are calculated for Eu^{3+} and TEMPTMA respectively. As a result, the adopted Eu^{3+}/TEMPTMA-based aqueous redox flow battery system exhibits good performance, reversibility and stability such as >99.97% per cycle (>99.88% per day) discharge capacity within containing 0.25 M Eu^{3+} in 1 M KCl as negolyte at 120 cycles and 29 days battery testing against little excess of 0.5 M TEMPTMA in 1 M KCl as posolyte.

Keywords: Aqueous redox flow battery, Hybrid system, Europium, TEMPTMA, Neutral pH.

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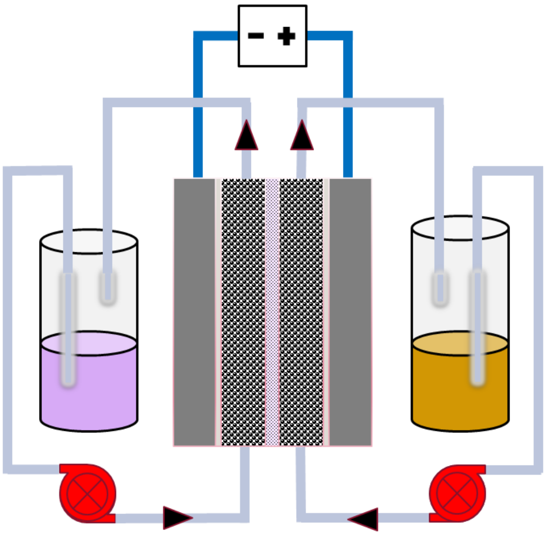
1. INTRODUCTION

Energy arrangements are essential for governments to make strides the environment and decrease their reliance on remote vitality sources (1). In this manner, renewable vitality frameworks are accepting more consideration than ever. On the other hand, vitality capacity gadgets can guarantee the long-term maintainability of renewable energies (2).

Redox flow batteries (RFBs) are a striking innovation course among existing vitality capacity frameworks (3). These batteries have a structure where electrolyte arrangements are put away in two partitioned tanks and vitality is delivered through chemical responses in one cell when it is compared to traditional batteries (4). One of the greatest preferences of RFBs is that their vitality and control capacities can be scaled autonomously which is of course related to the utilized chemicals in such battery frameworks (5). Integration with renewable energy sources such as solar power and/or wind power, RFBs may give long term applications with higher/longer vitality capacities as extraordinary advantage (6). There is also a calculate that creates it troublesome for such vitality capacity framework to be commercially far reaching due to utilized chemicals´ costs and components in case of large-scale application (7).



Scheme 1: The schematic illustration of redox-flow battery system including power source, redox cell (electrodes, ion exchange membrane, current collectors), reservoirs, tubing and pumps.

Aqueous redox flow batteries (ARFBs) are defined as water-based electrolytes to store and release energy (8). Non-aqueous redox flow batteries (NARFBs) are defined as organo-solvent based electrolytes (9). Water-based electrolytes provides superior energy and higher ionic conductivity in redox forms. In addition, the low cost and easy accessibility of water and salts make these batteries economical and non-flammability also increases safety in utilize (10). All properties can be numbered as their points of interest in comparison to non-aqueous RFBs, aqueous RFBs are more naturally promising (11).

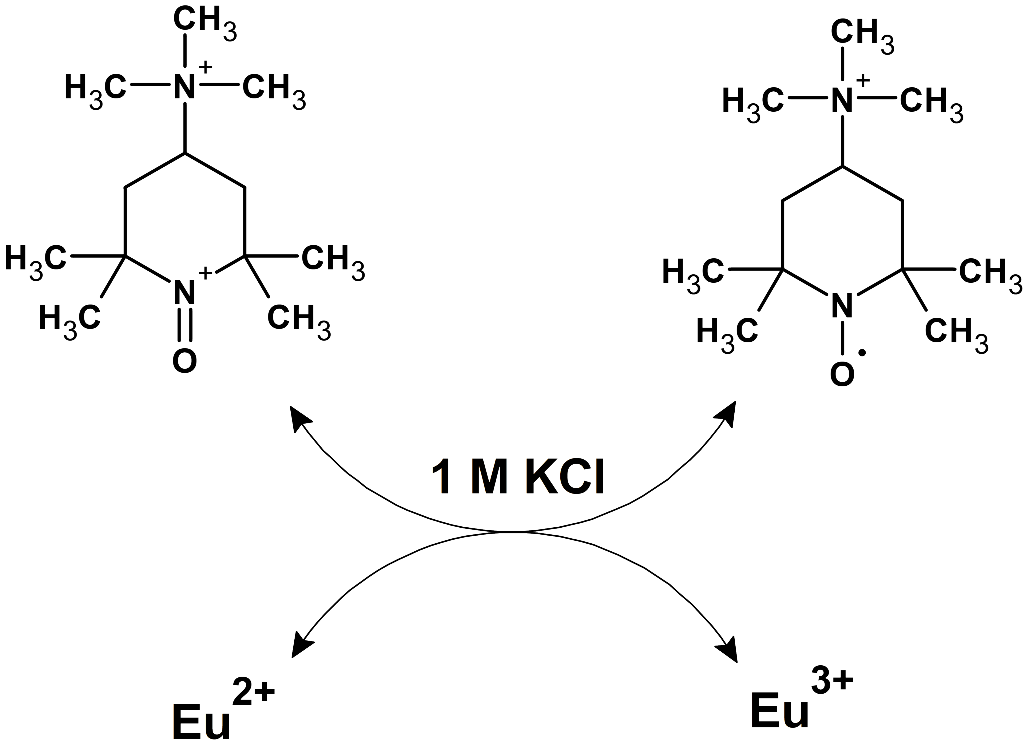
A greater variety of chemicals are available through hybrid redox flow batteries (HRFBs), which integrate both organic and inorganic components (12). This gives you additional choices for enhancing battery performance. Generally speaking, hybrid systems provide a better energy density than pure systems. In particular, hybrid systems have great promise for integrating renewable energy sources. More energy storage capacity results from this (13). However, depending on the chemical combinations used, hybrid batteries may also be more affordable. In general, organic components are less expensive than inorganic ones, and overall expenses can be decreased by combining them (14). Longer life and improved chemical stability can be obtained by combining the benefits of both organic and inorganic components in these hybrid systems. All things considered, hybrid redox flow batteries are versatile and may be tailored to meet a range of energy storage requirements (15).

Europium is one of the rare lanthanide group metals (16). It has been suggested to be used in aqueous redox flow batteries in the literature due to its relative electrochemical stability, reversibility and its reasonable production amount and cost when compared to traditional vanadium-based redox flow batteries (16,17). Eu^{3+}/Eu^{2+} reduction can be comparable with other redox-active species (Table 1).

Table 1: Potential and role comparisons of redox-active species in aqueous media.

Redox-active species	Potential (V vs SHE)	Posolyte/Negolyte
dMe-Vg^{2+}	-0.45	Negolyte
Eu^{3+}	-0.36	Negolyte
bPpN$(Me)_3$-Vg^{2+}	-0.33	Negolyte
V^{3+}	-0.25	Negolyte
$[Fc\text{-}CH_2N(Me)_3]^+$	+0.61	Posolyte
Fe^{2+}	+0.77	Posolyte
$TEMPTMA^+$	+0.98	Posolyte
VO^{2+}	+1.00	Posolyte

In this study, a Eu^{3+}/TEMPTMA-based which adopts one-electron battery system at 1.35 V in neutral pH containing 1 M KCl media is tested (Scheme 2). During battery and electrochemical studies, capacity change, charge-discharge and coulombic efficiencies are examined, and diffusion constant (D_0) values are calculated for Eu^{3+} and TEMPTMA respectively.



Scheme 2: The schematic illustration of redox reactions between TEMPTMA radical as posolyte and Eu^{3+} as negolyte in 1 M KCl as common electrolyte.

2. MATERIALS AND METHODS

Europium oxide (99.9%) was purchased from Alfa Aesar, Germany (Thermo Fisher Scientific), and TEMPOL (99%) was purchased from Jinan Refined Chemicals, China. Dimethylamine (DMA) and $AgNO_3$ was purchased from Sigma-Aldrich (Merck), Germany. Iodomethane (99.5%) was purchased from Acros Organics, Spain (Thermo Fisher Scientific). Other chemicals and supplements were obtained from VWR, Finland. AgCl was prepared by addition excess KCl to $AgNO_3$ solution in water. AgCl was suspended in isopropanol and covered with aluminum foil. TEMPTMA and $EuCl_3$ were prepared in accordance to designed synthetic methodologies (see supporting information).

All cyclic voltammetry analyses were performed using a PalmSens 4 potentiostat with PSTrace software from PalmSens BV (the Netherlands) using 2 mm glassy carbon disk electrode as working electrode (WE), 0.5 mm Pt wire as counter electrode (CE), and Ag/AgCl in 3.5 M KCl as reference electrode (RE). 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 working electrode was polished with 0.25 µm diamond powder (Büehler) and rinsed with distilled water during each measurement.

The EPR measurements were performed using Bruker Magnettech MS5000X on X-band (9.4 GHz) at room temperature with a typical organic radical adjustment setup for microwave power (10-20 mW) and magnetic field (200 – 650 mT) in quartz capillary which were sealed then with special plastic rubbers up and down. The resulting spectrum was processed using ESRStudio software and Origin.

3. RESULTS AND DISCUSSIONS

Before performing battery experiments, regular cyclic voltammetry analyses were run for Eu^{3+}, TEMPTMA, and a mixture of Eu^{3+}/TEMPTMA solutions to check reversibility and electrochemical compabilities. The cyclic voltammogram of mixture of Eu^{3+}/TEMPTMA also gave us understanding on detection of the battery voltage which is found to be 1.35 V (Figure 1).

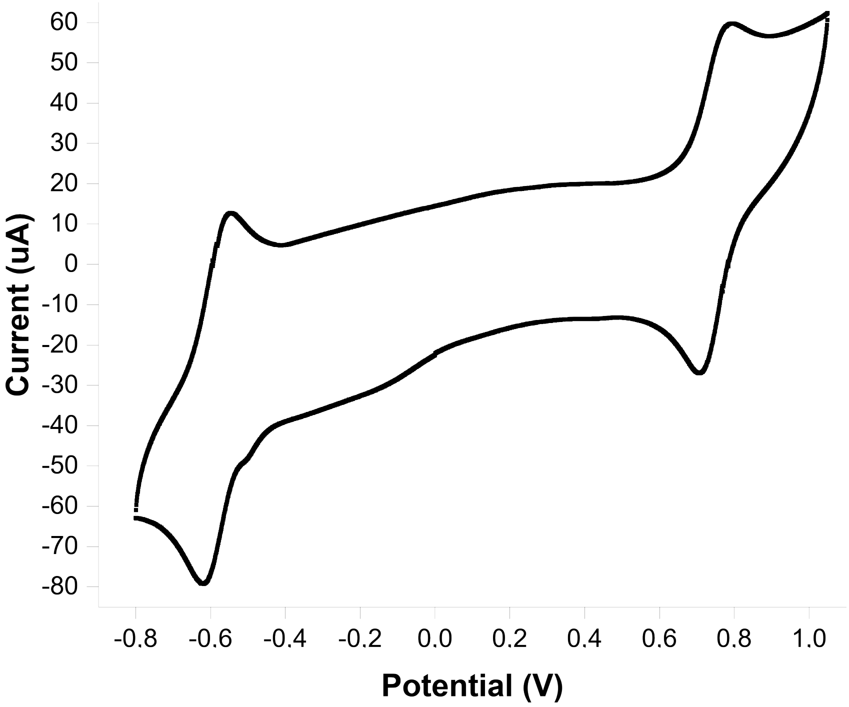


Figure 1: The cyclic voltammogram of mixture of Eu^{3+}/TEMPTMA in 1 M KCl using glassy carbon as working electrode (WE), Pt wire as counter electrode (CE) and Ag/AgCl in 3.5 M KCl as reference electrode (RE), scan rate: 100 mV/s.

A slightly capacity decay occurred at the early stages of the battery testing and after a while, the battery was stabilized and discharge capacity was slowly recovered to reach the certain amount to be restored (Figure 2). This could be explained that Eu(III) and Eu(II) ions can be found in various structures such as altered aqua and chloro complexes and those molecular rearrangements are more certain without decomposition. After 120 cycles within applying 100 mA current, charging at 1.35 V and applying 50 mA current, discharging at 0 V currents around 29 days, the battery system and the capacity are preserved successfully.

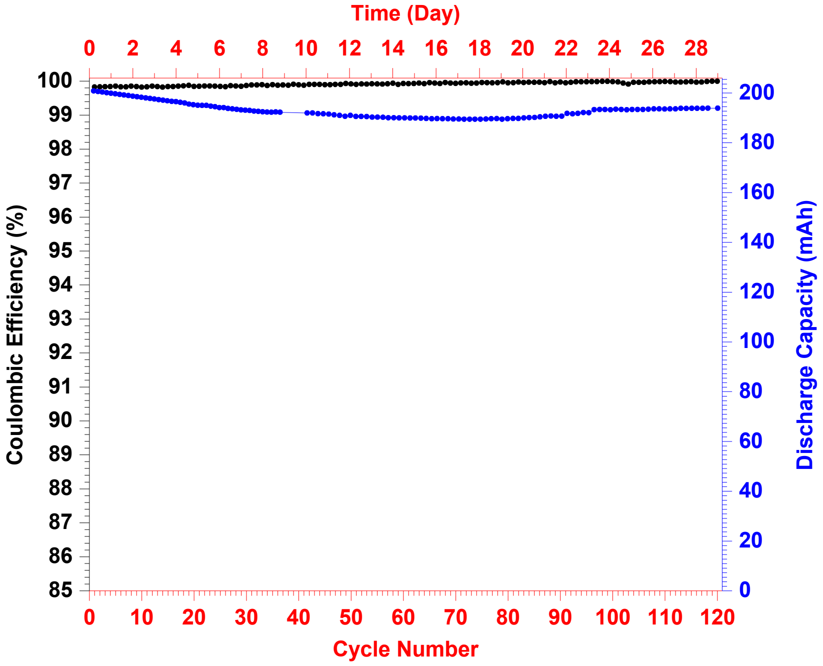


Figure 2. The experimental Coulombic efficiency and discharge capacity profile by day-based time and cycle numbers.

Additionally, we also tested self-discharge which was not considered in previous studies (17,18). In order to test self-discharge phenomenon, we tested our battery system for 5 hours period after being charged to Eu(II) to be found self-discharge 0.25 M Eu^{3+} in 1 M KCl is 0.0023% per hour, 0.0552% per day (Figure 3).

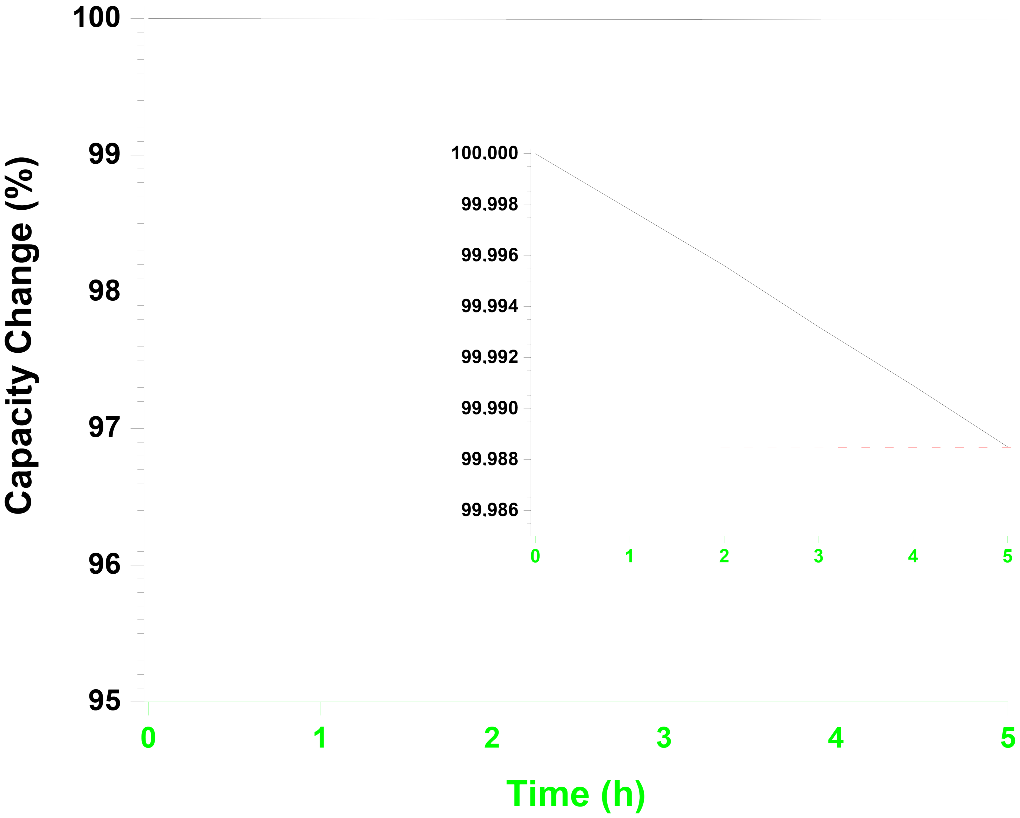


Figure 3: The self-discharge observation profile after charging at a certain time and rest mode for 5 hours.

It is concluded that Eu^{3+}/TEMPTMA-based one-electron battery system at 1.35 V in neutral pH containing 1 M KCl media showed good cycling performance. Our results were further compared with other Eu^{3+} batteries (16,17).

4. CONCLUSIONS

In conclusion, a hybrid aqueous redox flow battery of Eu^{3+} was tested as a negolyte material against $TEMPTA^{+}$ as a posolyte material in neutral pH 1M KCl supporting electrolyte. Eu^{3+}-based this 1.35 V redox flow battery system showed a good stability and reversibility under these circumstances. Self-discharge phenomenon was also considered and it found to be negligible as the charged-state battery is stable. The preliminary cost analyses also made to be compared regarding vanadium and Li-based batteries. As a results, Eu(III) ions are promising for long-term redox flow battery applications as compared to other heavy metals, europium is relatively non-toxic substance which carries no important biological role in living organisms.

5. ACKNOWLEDGMENTS

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6. CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

7. AUTHOR CONTRIBUTIONS

A. T.: conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, writing—original draft preparation, writing—review and editing.
P. P.: conceptualization, supervision, validation, writing—review and editing.

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