Journal of Basic and Environmental Sciences

ISSN
Online:2356-6388
Print:2536-9202

Research Paper Open Access

Studying the effect of adding thiourea to HFE on Mg-S battery behavior and its properties

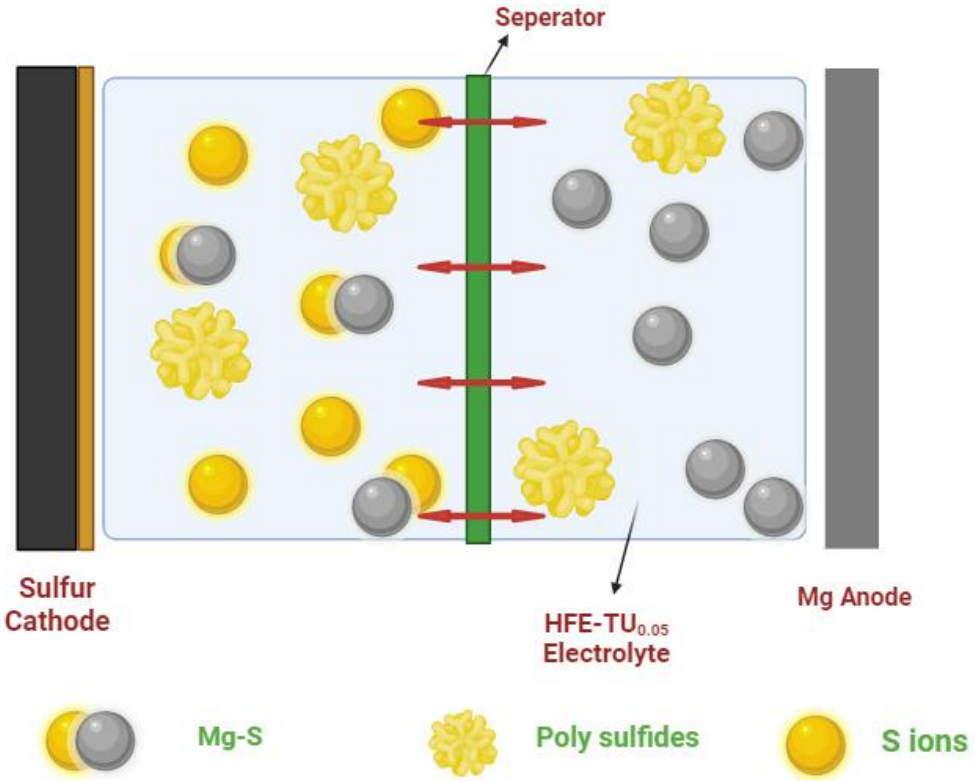
[1]Engy El-Dek; [2]Eslam sheha; [1]Alaa S Amin

[1]Chemistry Department, Faculty of Science, Benha University, 13518 Benha, Egypt

[2]Physices Department, Faculty of Science, Benha University, 13518 Benha, Egypt

Abstract:

The prolonged longevity of magnesium-sulfur batteries (Mg-S) with high energy density is still impeded by the slow kinetics of sulfur reduction and evolution and the severe polysulfide (PS) shuttling. Herein, improve of the Mg-S battery was tried by using thiourea (TU) as an additive to the halogen free electrolyte (HFE) which based on dissolving $Mg(NO_3)_2.6H_2O$ to acetonitrile and ethylene glycol dimethyl ether (ACN: G4). The erosion of the magnesium layer and the inability of magnesium ions to reach the cathode in significant quantities during the charging and discharging process are two frequent battery problems. Consequently, thiourea was applied as a corrosion inhibitor, allowing magnesium ions to pass through while also creating a protective layer on the anode's surface. From the electrochemical tests, Mg||Mg symmetric cells it can be observed that the most plating|stripping ratio of TU in HFE is HFE-$TU_{0.05}$ in 100 h. cycling. Mg|HFE-$TU_{0.05}$|MoS_2 cells were analyzed during the discharge/charge process. It was observed that HFE-$TU_{0.05}$ improve the cycling capacitance and coulombic efficiency (CE%) . The post-mortem analysis applied for the analysis of cathodes in the discharge and charge cells.



Scheme 1: Illustration discharge reaction mechanism in Mg-S battery

1. Introduction

The magnesium-sulfur (Mg-S) battery is garnering significant research interest due to its high theoretical energy density, cost-effectiveness, and the use of sustainable electrode materials.[1-2] However, the Mg-S batteries suffer from the low practical energy density mainly arising from the rapid dissolution of polysulfides and slow reaction kinetics between Mg and solid-phase sulfur.[3-4-5] The chemistry of magnesium-sulfur (Mg-S) batteries circumvents the challenges associated with intercalation by utilizing conversion reactions, leading to an enhanced theoretical specific capacity of 1673 mA h g^{-1}.[6] Thiourea functions as an electrolyte additive with dual roles. It acts as a redox mediator, facilitating the reduction of the activation energy barrier associated with lithium sulfide (Li_2S), while also serving as a shuttle inhibitor to reduce the phenomenon of polysulfide shuttling.[7] Thiourea-based ionic liquids serve as electrolyte additives to improve both cell safety and electrochemical performance. These additives contribute to the formation of a protective layer on the surfaces of electrodes, referred to as the solid electrolyte interface (SEI), thereby enhancing cycling performance and discharge capacities.[8-9] Herein, thiourea is used as additive to modify and enhance the chemical properties of halogen free electrolyte

(HFE), which composed of acetonitrile: Tetraglyme (ACN: G4) according to ref.[10]

2. Experimental Technique

Halogen free electrolyte was synthesized by dissolving 1.5 gm of $Mg(NO_3)_2.6H_2O$ in 5.7 ml of acetonitrile : 2.7 ml of Tetraglyme according to ref.[10] 0.05, 0.1, 0.15, 0.2 gm are added to 2 ml HFE with stirring for 24 hours. The XRD pattern was recorded for the collected electrodes from the half and full cells using the Rigaku MiniFlex 600 diffractometer with Cu Kα- radiation. SEM images were recorded using a Jeol JMS-700 equipped with energy-dispersive. UV−vis was conducted using an Edinburgh DS5 Dual Beam UV−vis spectrophotometer. ATR-FTIR spectroscopy was conducted using a BrukerAlpha II spectrophotometer.

3. Results and Discussion

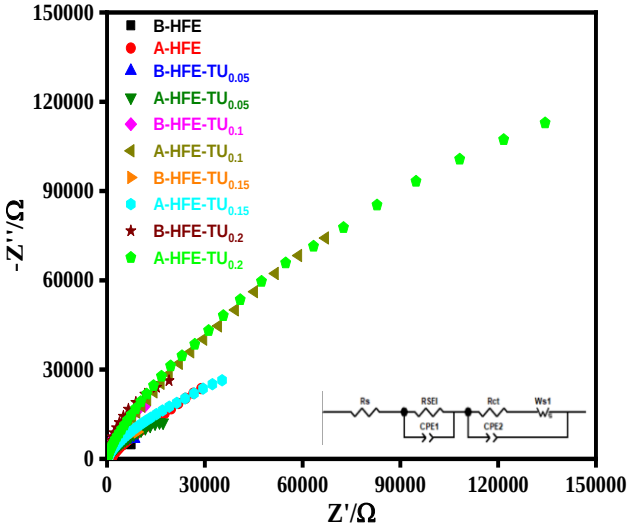


Figure 1: Nyquist Plot of Mg||S||Mg cells of HFE, and HFE-TU_x.

Figure 1 shows Nyquist plot of Mg||S||Mg of HFE, and HFE-TU_X cells before and after stripping/plating test. The equivalent circle inset is refers to the electronic element parameters which fitted using Z-View software. The components of the equivalent circuit are Rs, R_{SEI}, R_{ct}, CPE, and W_s, which refers to solution resistance, solid electrolyte interface resistance, charge transfer resistance, constant phase element capacitor, and werburg resistanse, respectively.

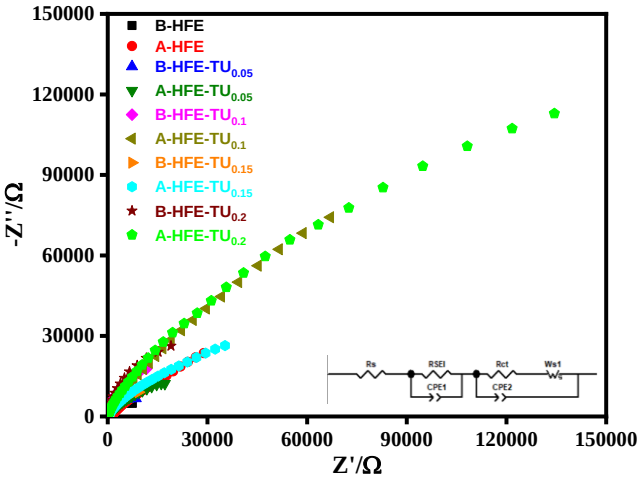


Figure 2: Mg Stripping/ plating of HFE, and HFE-TU_x

Figure 2 shows Mg||S||Mg cells which explain the time/voltage plot for HFE, and HFE-TU_x at 0.02 mA cm^{-2} with half/half hour DCH/CH parameters. The most-long term cycling capability is HFE-$TU_{0.2}$. Stripping/plating refers to the deposition/dissolution processes for Mg anode.

$$Mg\ (metal) \rightarrow Mg^{2+}+2e^{-}$$

$$Mg^{2+}+2e^{-} \rightarrow Mg\ (metal)$$

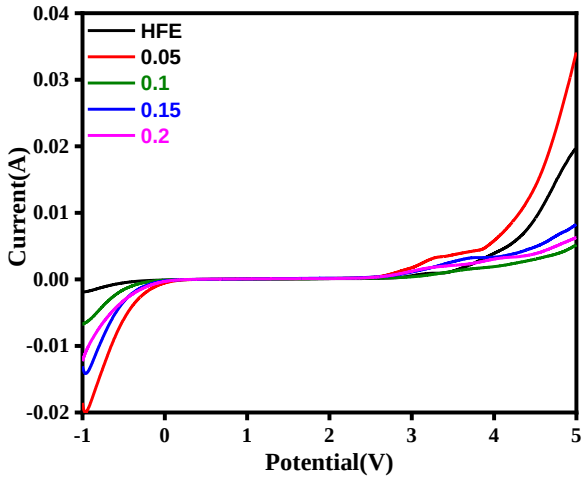


Figure 3: Linear sweap voltammetry of HFE, and HFE-TU$_x$

Figure 3 shows linear sweep voltammetry (LSV) of HFE, and HFE-TU$_x$ of Mg||S||SS cells. Linear Sweep Voltammetry is a fundamental electrochemical technique for characterizing battery components and understanding the energy, steadiness, and by and large execution of a battery framework. From the graph, it shows the long stability of HFE, and HFE-TU$_x$.

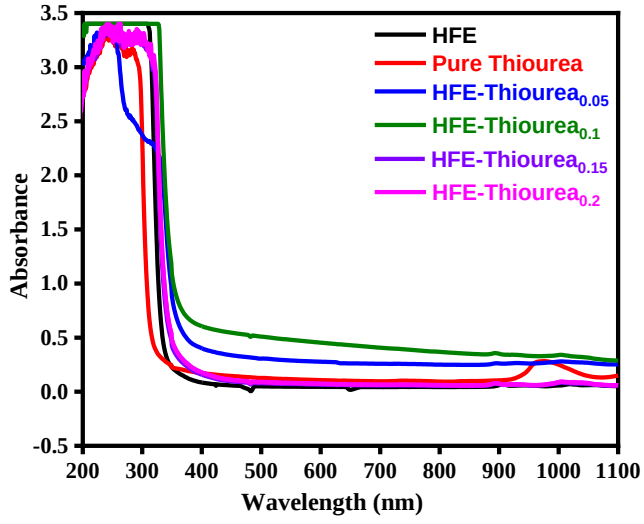


Figure 4: UV – visible plot of Pure Thiourea, HFE-Thiourea$_X$

Figure 4 shows UV-Visible which express the relation between wavelength and absorbance, it is observed that pure thiourea has an absorption peak at ~980 nm wavelength and ~ 0.4 a.u. absorbance. By adding thiourea in HFE, it is observed that HFE-Thiourea$_{0.1}$ has the most absorbance, However, HFE-Thiourea$_{0.05}$ has peak of absorbance at ~ 250 nm and ~ 3.3 a.u.

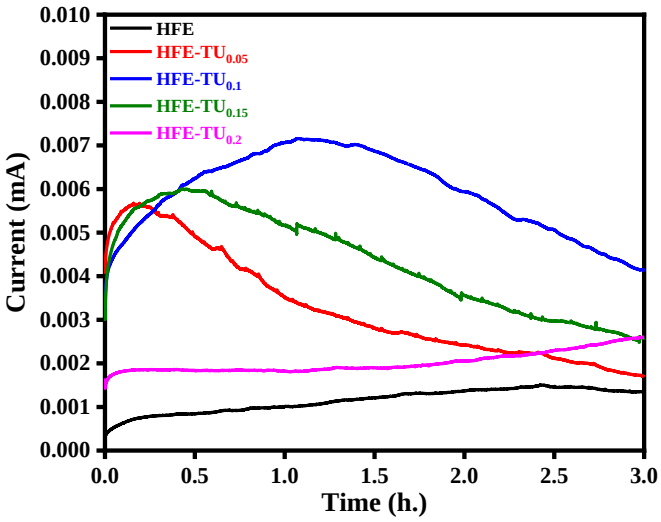


Figure 5: Polarization current curve vs time.

Figure 5 shows the current vs time which express the ion transference of Mg^{2+} ions of Mg||S||Mg cells for HFE, and HFE-TU$_x$. It was observed that HFE-TU$_{0.1}$ and HFE-TU$_{0.15}$ has the most current value of ~0.007 mA and ~ 0.006 mA, where the initial current for them are ~ 0.0035 mA, and ~ 0.003 mA, respectively. The most moderating current vs time for the HFE-TU$_x$ is with HFE-TU$_{0.05}$, where it records an initial current of ~ 0.004 mA to which gradually increases to ~ 0.0057 mA among ~ 0.25 h.

4. Concolusion

In conclusion, research on magnesium batteries utilizing thiourea as an electrolyte additive to HFE highlights a promising pathway for developing more sustainable and safer alternatives to traditional lithium batteries. Magnesium offers high energy storage capacity and density, paving the way for batteries with extended energy capacity and longer lifespan, while thiourea significantly enhances chemical stability and ionic transport efficiency within the battery. However, technical challenges remain, such as improving electrolyte performance and developing compatible anodes and cathodes to work efficiently together. These batteries represent advanced and scalable research areas to meet the growing demand for sustainable energy in industrial and personal applications.

5. References

(1) Bosubabu, D.; Li, Z.; Meng, Z.; Wang, L.-P.; Fichtner, M.; Zhao-Karger, Z. Mitigating self-discharge and improving the performance of Mg–S battery in Mg [B (hfip) 4] 2 electrolyte with a protective interlayer. Journal of Materials Chemistry A **2021**, 9 (44), 25150-25159.

(2) Zhang, Z.; Wang, B.; Ju, S.; Wu, Z.; Yang, Y.; Pan, H.; Yu, X. Progress and prospects for solving the" shuttle effect" in magnesium-sulfur batteries. Energy Storage Materials **2023**, 102933.

(3) Muthuraj, D.; Pandey, M.; Krishna, M.; Ghosh, A.; Sen, R.; Johari, P.; Mitra, S. Magnesium polysulfide catholyte (MgSx): synthesis, electrochemical and computational study for magnesium-sulfur battery application. Journal of Power Sources **2021**, 486, 229326.

(4) Luo, T.; Wang, Y.; Elander, B.; Goldstein, M.; Mu, Y.; Wilkes, J.; Fahrenbruch, M.; Lee, J.; Li, T.; Bao, J. L. Polysulfides in Magnesium-Sulfur Batteries. Advanced Materials **2024**, 36 (7), 2306239.

(5) Yang, Y.; Yang, H.; Wang, X.; Bai, Y.; Wu, C. Multivalent metal–sulfur batteries for green and cost-effective energy storage: Current status and challenges. Journal of Energy Chemistry **2022**, 64, 144-165.

BuFs-REC-2024-102Chm

(6) Zhao-Karger, Z.; Liu, R.; Dai, W.; Li, Z.; Diemant, T.; Vinayan, B.; Bonatto Minella, C.; Yu, X.; Manthiram, A.; Behm, R. J. r. Toward highly reversible magnesium–sulfur batteries with efficient and practical Mg [B (hfip) 4] 2 electrolyte. ACS energy letters **2018**, 3 (8), 2005-2013.

(7) Rafie, A.; Pai, R.; Kalra, V. A dual-role electrolyte additive for simultaneous polysulfide shuttle inhibition and redox mediation in sulfur batteries. Journal of Materials Chemistry A **2021**, 9 (47), 26976-26988.

(8) Chatterjee, K.; Pathak, A. D.; Sahu, K. K.; Singh, A. K. New Thiourea-based ionic liquid as an electrolyte additive to improve cell safety and enhance electrochemical performance in lithium-ion batteries. ACS omega **2020**, 5 (27), 16681-16689.

(9) Kim, K.; Ma, H.; Park, S.; Choi, N.-S. Electrolyte-additive-driven interfacial engineering for high-capacity electrodes in lithium-ion batteries: promise and challenges. ACS Energy Letters **2020**, 5 (5), 1537-1553.

(10) Sheha, E.; Farrag, M.; Fan, S.; Kamar, E.; Sa, N. A simple Cl–-free electrolyte based on magnesium nitrate for magnesium–sulfur battery applications. ACS Applied Energy Materials **2022**, 5 (2), 2260-2269.