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An effective dual electrolyte designed to enhance the performance of magnesium/sulfur batteries.

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Abstract

Magnesium batteries still encounter significant hurdles in their advancement, including issues like rapid loss of capacity, absence of suitable electrolytes, passivation of the magnesium anode, sluggish conversion reactions, and self-discharge. In this study, we substitute the conventional electrolyte with a dual layer and investigate the electrochemical properties in Magnesium/Sulfur battery. This dual electrolyte comprises two layers: one derived from a simple halogen-free electrolyte (HFE) and another from a polymer layer interface (PLI). The HFE consists of magnesium nitrate ($Mg(NO_3)_2$), magnesium triflate ($Mg(CF_3SO_3)_2$), and succinonitrile (SN) dissolved in acetonitrile (ACN)/tetraethylene glycol dimethyl ether (G4) cosolvents, supplemented with dimethyl sulfoxide as a functional additive. The PLI, on the other hand, incorporates polyvinylidene fluoride (PVDF), SN, and ($Mg(CF_3SO_3)_2$), dissolved in methyl-2-pyrrolidine (NMP)/G4 cosolvents, aimed at insulating the Mg anode surface from the liquid electrolyte. The dual electrolyte demonstrates promising characteristics including high ionic transference number ($t_{mg^{+2}} = 0.9$), excellent oxidation stability, low overpotential, and consistent Mg stripping/plating for up to 100 hours. The Mg/S full cell exhibits an impressive initial discharge/charge capacity of approximately 1312/432 mAhg^{-1}.

Keywords: Magnesium/Sulfur battery; Dual electrolyte; specific capacity

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1. Introduction

Energy storage devices play very important roles in the management and storage of renewable energy [1]. Among these, magnesium batteries have emerged as highly promising post-lithium batteries owing to their advantageous characteristics such as a low reduction potential, affordability, safety, high theoretical energy density, and dendrite-free behavior [2, 3]. Numerous efforts have been made to explore the compatibility of various cathodes and electrolytes with magnesium anodes [4]. Sulfur (S), being abundant in the earth's crust, non-toxic, and possessing a high theoretical specific capacity, presents itself as an excellent electrode material [5]. However, the utilization of Mg/S batteries faces obstacles related to electrolytes. The majority of electrolytes used in rechargeable magnesium batteries are nucleophilic and tend to react with sulfur cathodes due to their strong reductive nature, thereby forming a passivation layer on the surface of the Mg anode [6].

Lately, there have been advancements in non-nucleophilic electrolytes, like $Mg(HMDS)_2$ [7], MACC [8], $Mg(TFSI)_2$ [9], and $Mg[B(HFP)_4]_2$ [10]. These electrolytes offer benefits such as high Coulombic efficiency, minimal polarization, and strong anodic stability. However, their practical use is hindered by challenges like low efficiency in plating and stripping, short cycling lifespan, complex preparation procedures, and high costs. Additionally, conventional liquid electrolytes like magnesium bis(trifluoromethanesulfonimide), magnesium trifluoromethanesulfonate, magnesium hexafluorophosphate, and magnesium perchlorate salts lead to the formation of a passivation layer on the Mg anode surface, which greatly impacts the performance of Mg batteries. Moreover, in liquid electrolytes, the bivalent nature and high charge density of Mg2+ ions promote the formation of ion pairs, restricting ionic conductivity and causing adverse interfacial effects [11].

Utilizing a dual electrolyte approach, as opposed to conventional methods, has significantly improved the sulfur battery's performance [12]. This dual electrolyte configuration comprises two distinct layers: firstly, a liquid electrolyte such as a halogen-free electrolyte (HFE), and secondly, a polymer layer interface (PLI). The introduction of HFE, which demonstrates compatibility with Mg metal and exhibits superior oxidative stability compared to ether solvents, marks a notable advancement due to its inert and non-corrosive properties. Meanwhile, the PLI serves as a protective barrier, aimed at isolating the Mg anode surface from the liquid electrolyte, thereby reducing the formation of the passivation layer and enhancing battery performance [13].

In response to the mentioned challenges, this research endeavors to employ a dual electrolyte approach and examine its effectiveness in Mg/S batteries. The halogen-free electrolyte (HFE) is formulated using components like $Mg(NO_3)_2$, $Mg(CF_3SO_3)_2$, SN, and DMSO, while the polymer layer interface (PLI) comprises PVDF, SN, and $Mg(CF_3SO_3)_2$. The performance evaluations of the cell are conducted at 55°C. The findings suggest that integrating a dual electrolyte system proves to be a promising strategy for enhancing the performance of Mg-S batteries.

2. Experimental

To acquire PLI, a mixture containing 5 grams of polyvinylidene fluoride (PVDF), 1.25 grams of SN, and 33wt.% $Mg(CF_3SO_3)_2$ dissolved in a blend of methyl-2-pyrrolidine (NMP) and G4 solvents is stirred for 48 hours. Afterwards, PE is applied onto glass sheets using an applicator and subsequently dried at 55 ºC in a vacuum oven.

To achieve HFE, a solution is prepared by dissolving 1.1 grams of preheated magnesium nitrate, $Mg(NO_3)_2.6H_2O$ (Alfa-Aesar 98%), along with 0.4 grams of magnesium triflate ($Mg(CF_3SO_3)_2$) (Alfa-Aesar), 0.03 grams of succinonitrile (SN), and 0.75 milliliters of DMSO in a mixture of acetonitrile (ACN) and tetraethylene glycol dimethyl ether (G4) solvents. The solution is then stirred for 24 hours [14].

The combination of HFE and PLI is indicated by the term "dual electrolyte."

Cathode

To produce the cathode, 1.35 grams of sulfur and 1.56 grams of carbon were finely ground and subjected to ball milling for 2 hours. Subsequently, they were heated at approximately 150 ºC in an autoclave for 2 hours. A mixture containing 0.85 grams of the S/C composite and 0.15 grams of PVDF dissolved in NMP was stirred for 24 hours. This mixture was then applied onto aluminum foil using a minicoater (MC-20, Hohsen) and dried in an oven at around 90 ºC for 2 hours. [15].

Scanning electron microscopy (SEM) coupled with an energy-dispersive X-ray spectroscopy (EDS) unit was conducted using a JSM-5600-LV instrument by JEOL LTD. Electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and cyclic voltammetry (CV) were carried out using a CHI604 electrochemical workstation. The impedance data obtained were analyzed using ZView software. CR2032 coin-type cells were assembled within an argon-filled glove box. The magnesium-ion transference number of the Mg/Dual/Mg cell was determined via AC impedance measurements before and after polarization at a voltage change of 0.1V. Discharge/charge tests were executed using a NEWARE BTS4000 tester within the voltage range of 0.1 to 2.5 V. Subsequently, the coin cells were disassembled, and the cathode disks collected were rinsed in acetonitrile (ACN) and then dried for 2 hours in an oven set to 90°C prior to SEM and EDS analyses.

3. Results and discussion

Linear sweep voltammetry (LSV) was employed to assess the oxidation resistance of the electrolyte in an SS/Dual/Mg coin cell, covering a voltage range of -1 to 5 V at 55°C (Fig. 1). The dual electrolytes exhibit significant oxidation stability extending up to 4.2 V, validating their substantial electrochemical stability window.

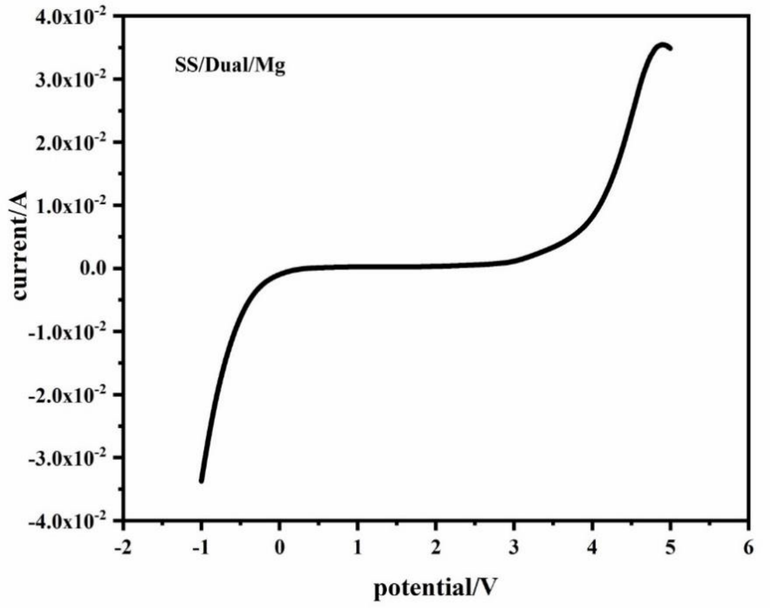

Fig. 1 Linear sweep voltammetry (LSV) for SS/Dual/Mg cell at 55 ºC

Determining the magnesium transference number ($t_{mg^{+2}}$) is a crucial technique for assessing the efficacy and rate capability of electrolytes in battery applications. This value can be calculated using Equation [16]:

$$t_{mg^{+2}} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)} \qquad (1)$$

Here, I_0 and I_s represent the initial and final currents, while R_0 and R_s denote the resistances of the cell before (B) and after (A) polarization, respectively. ΔV represents the DC voltage applied to polarize the sample. In Fig. 2(a, b), the impedance spectra before and after polarization, along with the variation of polarization current over time for the Mg/Dual/Mg cell at 55°C, are illustrated. The observed trend indicates a gradual decrease in current until reaching a steady state. Utilizing the aforementioned equation yields a value of $t_{mg^{+2}}$ as 0.9. This high value suggests that the dual electrolyte serves as an effective medium, facilitating the passage of Mg^{2+} ions with efficiency.

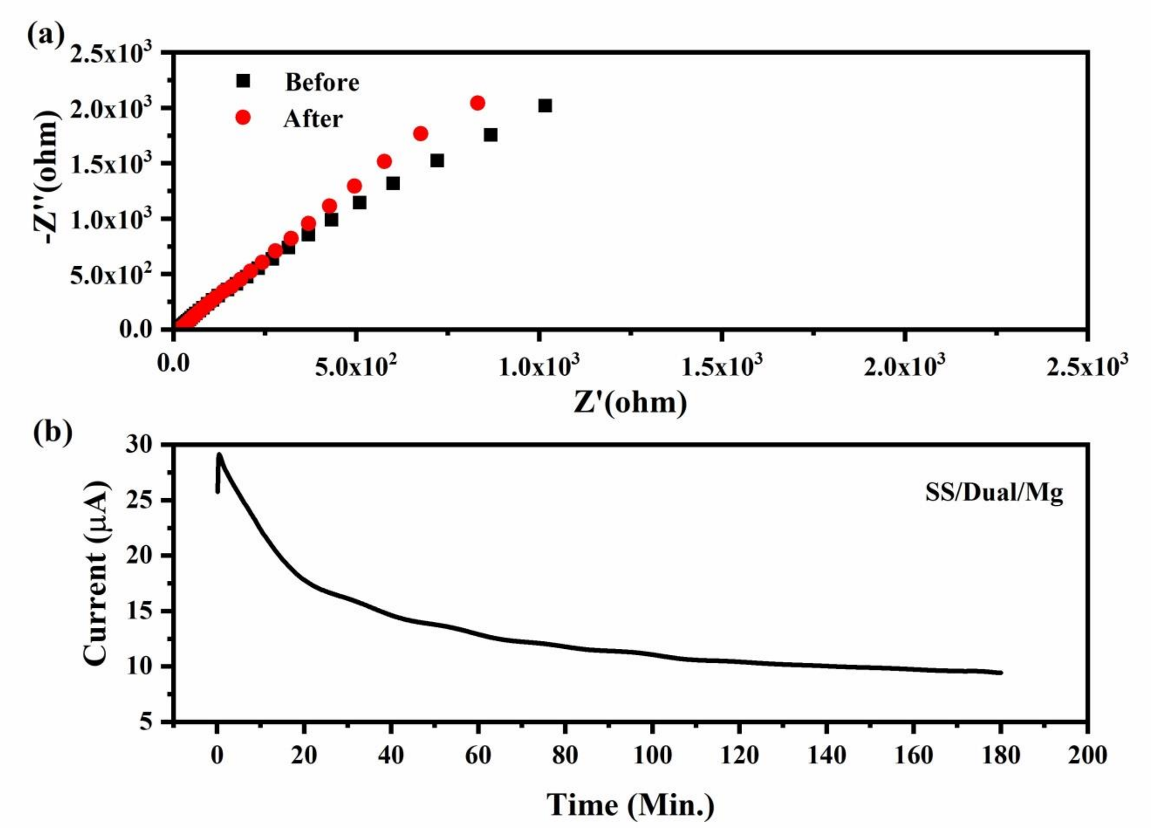

Fig. 2 (a) Nyquist plots before and after DC polarization, (b) DC polarization curve for Mg/Dual/Mg cell.

To examine the electrochemical stability of dual electrolytes, the reversibility of Mg plating and stripping processes was analyzed. Fig. 3 depicts the stripping-plating (SP) curves of Mg/Dual/Mg at a current density of 0.02 mA cm^{-2}. The incorporation of DMSO and $Mg(NO_3)_2$ significantly enhanced the stability of the electrolyte, resulting in minimal overpotential for up to 100 hours. This suggests their role in enhancing the passage of Mg ions through the dual electrolyte by promoting evolution at the anode/electrolyte interface at the surface of the Mg anode [17].

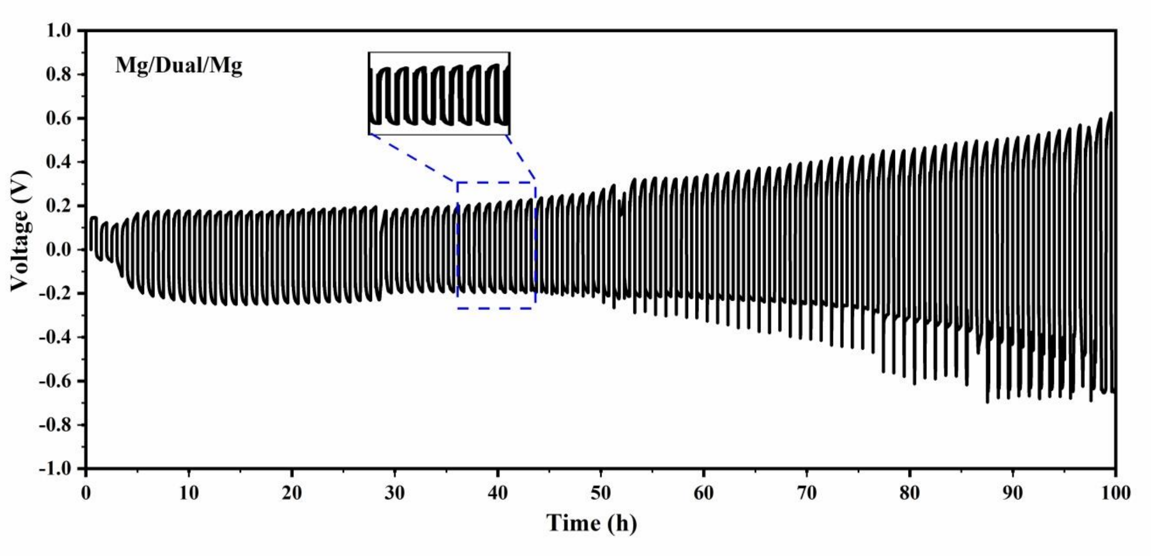

Fig. 3 Mg stripping/ plating (SP) for symmetric Mg/Dual/Mg cell (insets: amplified voltage profiles)

The cyclic voltammetry (CV) method was employed to assess the interaction between magnesium and sulfur during magnesium insertion/extraction within a potential range of 0.2-2.5 versus Mg/Mg^{2+} at a scan rate of 0.02 mV s^{-1} (Fig. 4). The CV curve exhibits a notable high current density, with a reduction peak observed at 0.28 V, indicative of the interaction between Mg^{2+} and S [12].

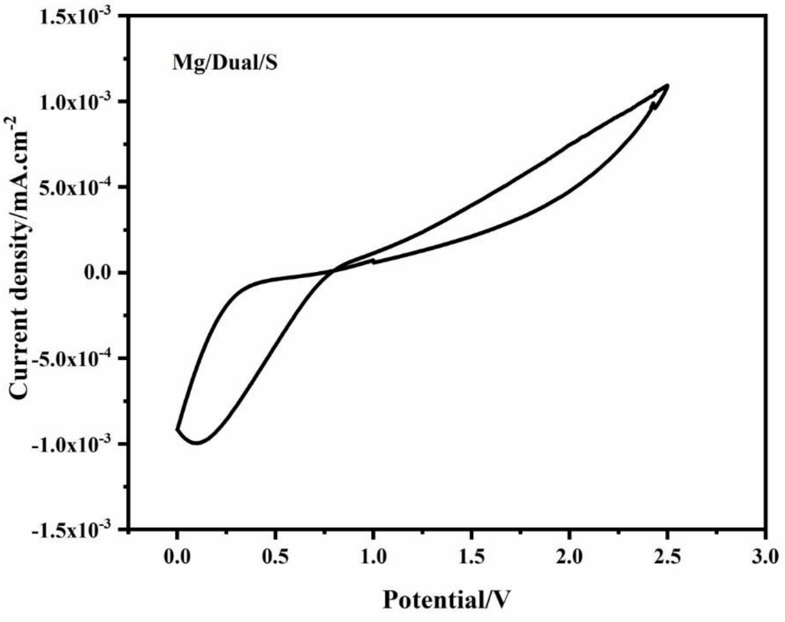

Fig.4 Cyclic Voltammetry (CV) for Mg/Dual/S cell

Figures 5(a, b) depict the Nyquist plots of the Mg/Dual/S cell, showcasing various parameters including the ohmic resistance of the bulk cell (R_b), the solid electrolyte interfacial resistance (R_{SEI}), the charge-transfer resistance (R_{ct}), and the Warburg factor (A_w). These were derived using the equivalent circuit as shown in the inset of Fig. 5a and by determining the slope of the linear fitting between Z and $\omega^{-0.5}$ at low frequencies (Fig. 5b). The diffusion coefficient of magnesium ions in the sulfur cathode ($D_{Mg^{+2}}$) for Mg/Dual/S was then calculated employing this equation [18]:

$$D_{Mg}^{2+} = \frac{R^2T^2}{2A^2n^4F^4C^2A_w^2} \qquad (2)$$

Here, R, T, A, n, F, and C represent the gas constant (8.314 J/mol K), temperature, the cathode area in contact with the electrolyte, the number of electrons involved, the Faraday constant, and the concentration of Mg^{2+} ions, respectively. The determined diffusion coefficient value, $D_{Mg^{+2}}$, amounts to 6.79×10^{-13} cm^2 s^{-1}, indicating facile and extensive diffusion of magnesium ions within the sulfur framework. This facilitates a notable enhancement in rate performance and other electrochemical characteristics [19].

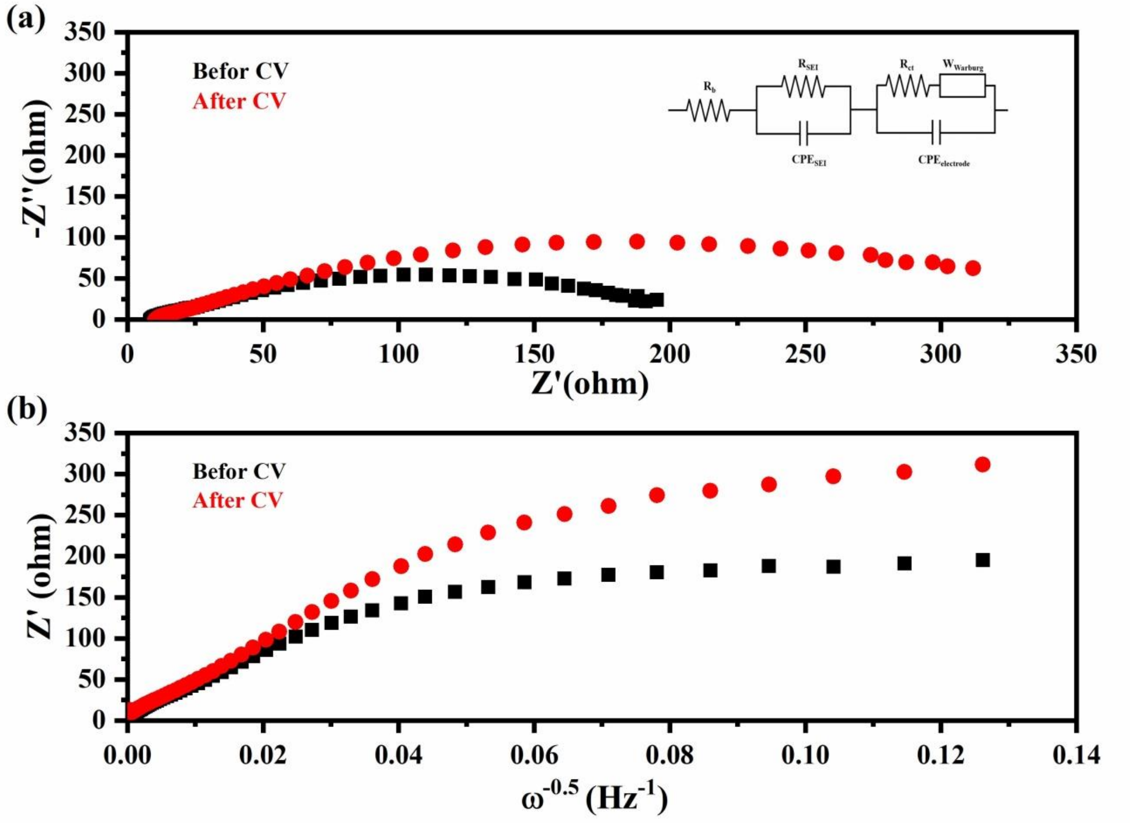

Fig.5 (a) Electrochemical impedance spectra (EIS), (b) Linear fitting of Warburg impedance for Mg/Dual/S cell

Figure 6 displays the initial cycle of galvanostatic discharge/charge curves for the Mg/Dual/S cell, conducted at room temperature (RT) and 55°C, with a current density of 0.02 mA g^{-1}. The cell exhibits an impressive initial discharge/charge capacity of 1312/432 mA h g^{-1}. Notably, the discharge curve features a plateau around ~0.86 V, likely attributed to the sequential insertion/extraction of Mg^{2+} ions into/from the sulfur framework via the conversion reaction: $Mg+S_8 \leftrightarrow MgS_n$ [20].

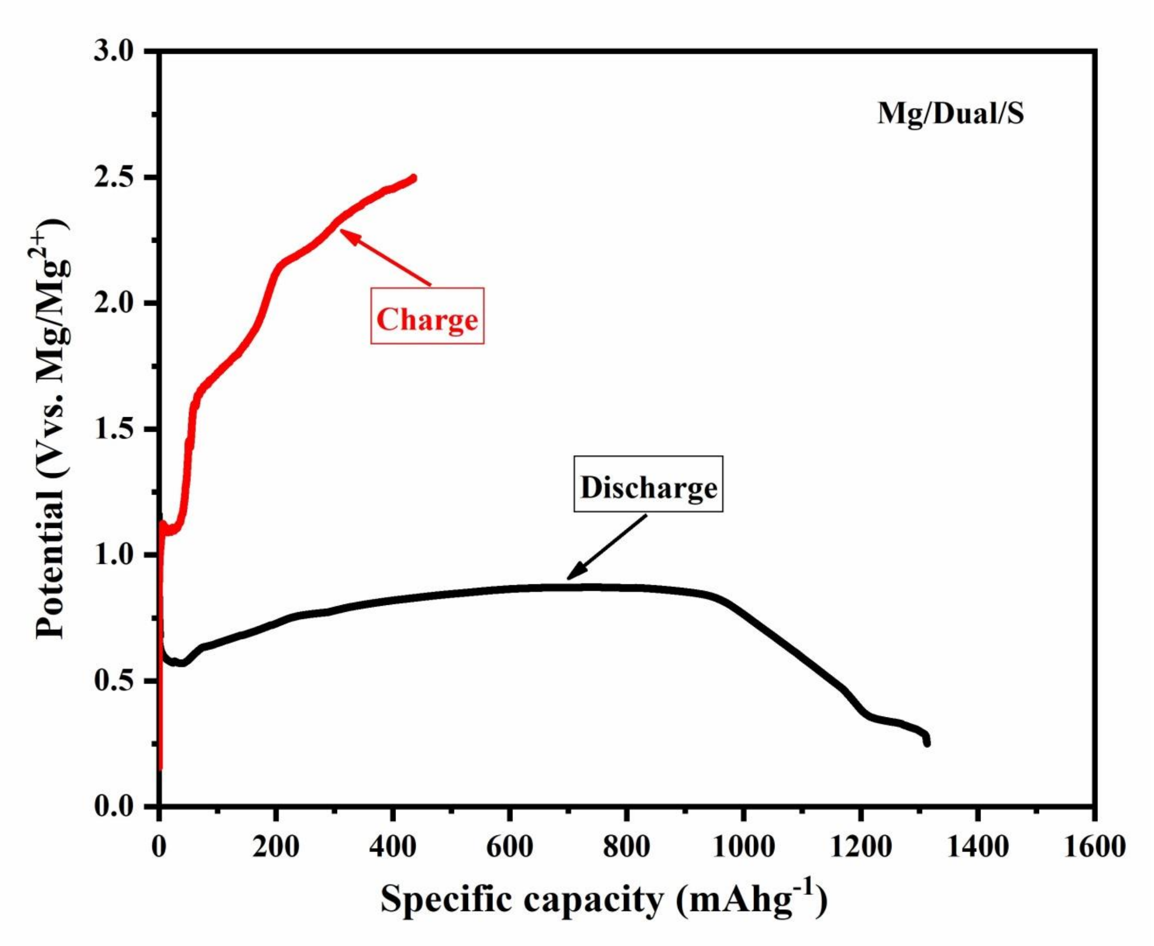

Fig.6 Charge-Discharge curve for Mg/Dual/S cell

4. Conclusion

This study highlights the importance of employing dual strategies to enhance the performance of Mg/S cells. By utilizing a dual electrolyte, the cell demonstrated notable achievements including a high ionic transference number ($t_{mg^{+2}}$ = 0.9), minimal overpotential, and stable Mg stripping/plating. The Mg/Dual/S cell prototype exhibited a substantial initial discharge/charge capacity of 1312/432 mA h g^{-1}, along with a diffusion coefficient $D_{Mg^{+2}}$ = 6.79×10^{-13} cm^2 s^{-1}. Postmortem analysis of sulfur cathodes at various electrochemical stages showcased the reversible movement of magnesium ions within the sulfur framework through the conversion reaction. These findings underscore the significance of this electrolyte system and the advancement of high-performance Mg/S batteries.

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