Ionic liquids are promising electrolytes for the primary Mg-air batteries. Three electrolytes, including pure 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide liquid, 50 mol.% butyl acetate and 50 mol.% water were studied. Attenuated total reflectance Fourier transform infrared spectroscopy, scanning electron microscopy and electrochemical impedance spectroscopy were used to examine discharge performance and the effects of butyl acetate and water additions. Galvanostatic measurements indicate that butyl acetate is an excellent additive, which can significantly improve the battery performance by reducing electrolyte impedance by increasing conductivity. However, while water also improved electrolyte discharge performance, it was consumed by the hydrogen evolution reaction over the 72 h discharge.

**Results and Discussion**

The galvanostatic discharge curves and the ATR-FTIR spectra of the electrolytes are shown in Fig. 1. The discharge current density was 0.1 mA/cm² in each case. As seen in Fig. 1a, the operating voltage rapidly decreased in the early discharge stage, caused by the internal resistance of the battery, and then reached an approximately constant value for the consequent 72 h. Compared with the IL mixture (H₂O and BA added separately), the discharge performance of pure PP¹₄TFSI exhibits instabilities, accompanied by lower voltage and more voltage fluctuations. Based on the discharge curves, H₂O and BA additions resulted in higher and more stable voltage.

In the initial 10 h of discharge, the voltage of PP¹₄TFSI with 50 mol.% H₂O electrolyte gradually increased and declined thereafter. Normally, during the discharge process, the hydrogen evolution reaction occurs at the Mg anode:

\[
\text{Mg} + \text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{H}_2 
\]

The consumption of H₂O and the accumulation of Mg(OH)₂ may cause high electrical resistance of the electrolyte, resulting in deteriorated battery performance after 10 h of discharge. In this study, the action mechanisms of H₂O on PP¹₄TFSI were analyzed in detail.
Figure 1. (a) Galvanostatic discharge curves and (b) ATR-FTIR spectra of electrolytes.

The discharge curve of the PP14TFSI with 50 mol.% BA exhibits minimum fluctuations and BA has an outstanding performance over the 72 h galvanostatic discharge period, suggesting that BA is a stable additive for the PP14TFSI.

As seen in Fig. 1b, the spectra from the original IL, IL after discharge and IL with added H2O after discharge look quite similar. The chemical structure of PP14TFSI didn’t change after 72 h discharge. This illustrates that PP14TFSI is a chemically stable electrolyte, which can withstand longer discharge. Lack of noticeable H2O peak between 3550 cm\(^{-1}\) and 3230 cm\(^{-1}\) in the discharged H2O-IL system implies that H2O is involved in the hydrogen evolution reaction. The PP14TFSI BA mixture results are similar to the original pure PP14TFSI. According to the BA-IL system spectra, the peak at 1728 cm\(^{-1}\) is assigned to the C=O bond of BA. The ATR-FTIR results of the BS-IL system confirmed the effects of BA on the stability of PP14TFSI.

To further investigate the impedance of the three systems, several equivalent circuits were constructed in Figs. 2b–2d. In Figs. 2b–2d, Rs represents the solution resistance, Rt and CPE or C are the charge transfer resistance and double layer capacitance of the Mg surface, and L is the inductance. W is the Warburg impedance, describing the diffusion process in pure IL electrolyte. The fitted values of the equivalent elements are listed in Table I. Low X² variance values reflect good fits of electrolyte impedance.

In Fig. 2b, the W element explains electric charge transfer difficulty in pure IL due to the enormous PP14TFSI ionic group size and high viscosity, causing large mechanical drag force. The lack of W element in Figs. 2c and 2d indicates that BA and H2O make charge transfer more effective. The effects of BA and H2O on viscosity is relatively low but still plays its role on the charge transfer.

In Table I, the Rs parameter values suggest that BA can significantly reduce the solution resistance, but H2O has no effect at all. Accordingly, the conductivity of the three electrolytes is shown in Fig. 3b, the evolution reaction during the discharge process. The capacitive loops in each electrolyte system are related to the interfacial electrochemical reactions and the interface charge transfer, although the capacitive loops of pure IL and BA-IL systems before discharge are incomplete. Noteworthy, sloped lines, which represent the diffusion process in the electrolyte, are obtained in the IL systems, indicating the difficulty of charge transfer in pure PP14TFSI.25

In Table I, the Rs parameter values suggest that BA can significantly reduce the solution resistance, but H2O has no effect at all. Accordingly, the conductivity of the three electrolytes is shown in Fig. 3b, the
Figure 3. (a) Viscosity of the three electrolytes; (b) Conductivity of the three electrolytes.

results are in correspondence with \( R_s \). Obviously, the consequences contradict to the coulomb force law:

\[
F = \frac{Q_1 Q_2}{4 \pi \varepsilon_0 \varepsilon_r r^2}
\]

where \( F \) is the electrostatic force, \( Q_1 \) and \( Q_2 \) are point electric charges, \( \varepsilon_0 \) is vacuum permittivity, \( \varepsilon_r \) is relative permittivity of the medium, and \( r \) is the distance between the two charges. The electrostatic force inhibits the electrolytic dissociation, and with high force, most of the ionic species exist as ion pairs. Ion pairs contribute neither ionic strength nor ionic conductivity to the solution.\(^{26}\) According to the coulomb force law, the electrostatic force of attraction between two ions with the opposite charge decreases with the increase of \( \varepsilon_r \). The permittivity of BA and H\(_2\)O is 5.07 and 78.36 F/m respectively,\(^{27}\) however, H\(_2\)O lost its proper role due to low solubility in IL. Thus it can be seen that both favorable miscibility and permittivity are necessary.

As for the interface processes, double layer capacitance \( C \) in pure IL in Fig. 2b is replaced by the CPE element in Figs. 2c and 2d, and the \( n \) parameter for the CPE is between 0.529 and 0.713 in Table I. This illustrates that H\(_2\)O and BA reduce the Mg anode interface stability. Moreover, it is noteworthy that H\(_2\)O decreases the charge transfer resistance by one order of magnitude, which can be observed by comparing the \( R_t \) values in each system, revealing that H\(_2\)O plays an essential role in the interface process of charge transfer. For the H\(_2\)O-IL system, H\(_2\)O improved the chemical properties of the interface between Mg anode and an organic electrolyte solution and then promoted the electrochemical process of charge transfer by extracting it from the anode and transferring it to the electrolyte. The difficult degree of the charge transfer also can be reflected by the SEM images of the Mg anode surfaces before and after 72 h discharge in pure IL, 50 mol.% BA-IL and 50 mol.% H\(_2\)O-IL electrolytes, as shown in Fig. 4. In contrast, more pronounced discharge morphology could be seen on the Mg surface of H\(_2\)O-IL in Fig. 4f, which corroborated the positive effect of H\(_2\)O on the electrode/electrolyte interface, accompanying inevitable self-corrosion. The round-like bulges in Fig. 4f suggest that there was gas generated at the interface during the discharge process, which further proves hydrogen evolution on the Mg surface in the H\(_2\)O-IL system. Beyond that, the wide and deep cracks on the electrode locally of BA-IL in Fig. 4e and the morphology in Fig. 4f agree with the inductance results in Fig. 2d, representing intergranular corrosion of the Mg anode.

### Table I. EIS elements values simulated using the corresponding equivalent circuits.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Pure IL Before</th>
<th>Pure IL After</th>
<th>BA-IL Before</th>
<th>BA-IL After</th>
<th>H(_2)O-IL Before</th>
<th>H(_2)O-IL After</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s ) ( \times 10^3 ), ( \Omega \cdot \text{cm}^2 )</td>
<td>2.699</td>
<td>3.102</td>
<td>0.27</td>
<td>0.809</td>
<td>3.552</td>
<td>3.389</td>
</tr>
<tr>
<td>CPE ( \times 10^{-5}, \text{F} \cdot \text{cm}^{-2} )</td>
<td>-</td>
<td>-</td>
<td>3.048</td>
<td>3.515</td>
<td>4.087</td>
<td>4.473</td>
</tr>
<tr>
<td>( n ) (0.0&lt;n&lt;1)</td>
<td>-</td>
<td>-</td>
<td>0.713</td>
<td>0.621</td>
<td>0.529</td>
<td>0.568</td>
</tr>
<tr>
<td>( R_t ) ( \times 10^5 ), ( \Omega \cdot \text{cm} )</td>
<td>6.109</td>
<td>2.84</td>
<td>3.738</td>
<td>1.231</td>
<td>0.173</td>
<td>0.479</td>
</tr>
<tr>
<td>( L ) ( \times 10^6 ), ( \Omega \cdot \text{cm}^2 )</td>
<td>-</td>
<td>-</td>
<td>5.332</td>
<td>-</td>
<td>2.049</td>
<td></td>
</tr>
<tr>
<td>( C ) ( \times 10^{-5}, \text{F} \cdot \text{cm}^{-2} )</td>
<td>4.576</td>
<td>5.315</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( W ) ( \times 10^{-5}, \text{F} \cdot \text{cm}^2 )</td>
<td>3.652</td>
<td>4.537</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Variance, ( X^2 ) ( \times 10^{-3} )</td>
<td>2.091</td>
<td>7.224</td>
<td>6.351</td>
<td>5.848</td>
<td>7.843</td>
<td>5.842</td>
</tr>
</tbody>
</table>

Figure 4. SEM micrographs of the Mg-anode in different electrolytes before and after 72 h discharge: (a) pure IL before, (b) BA-IL before, (c) H\(_2\)O-IL before, (d) pure IL after, (e) BA-IL after, (f) H\(_2\)O-IL after.
Further work is underway to research the mechanism and optimal dosage of additives. Obviously, the battery structure is also crucial and is currently under investigation.

Conclusions

Electrochemical performance of the \( \text{PP}_{14}\text{TFSI} \) ionic liquid, BA-IL and \( \text{H}_2\text{O}-\text{IL} \) mixtures as an electrolyte for the Mg-air battery was investigated. The \( \text{PP}_{14}\text{TFSI} \) ionic liquid can sustain 72 h discharge. BA increased the discharge voltage and made it more stable. Meanwhile, \( \text{H}_2\text{O} \) has a similar action, but the effect was degraded by the hydrophobicity at the interface between the anode and the electrolyte.

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