## Ambient Lithium–SO<sub>2</sub> Batteries with Ionic Liquids as Electrolytes\*\*

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**Abstract:** Li-SO<sub>2</sub> batteries have a high energy density but bear serious safety problems that are associated with pressurized SO<sub>2</sub> and flammable solvents in the system. Herein, a novel ambient Li-SO<sub>2</sub> battery was developed through the introduction of ionic liquid (IL) electrolytes with tailored basicities to solvate SO<sub>2</sub> by reversible chemical absorption. By tuning the interactions of ILs with SO<sub>2</sub>, a high energy density and good discharge performance with operating voltages above 2.8 V were obtained. This strategy based on reversible chemical absorption of SO<sub>2</sub> in IL electrolytes enables the development of the next generation of ambient Li-SO<sub>2</sub> batteries.

**L** nergy storage is of central importance for modern society.<sup>[1]</sup> The lithium–sulfur dioxide (Li-SO<sub>2</sub>) battery is a lightweight, long-life, high energy density primary battery in which cheap, abundant SO<sub>2</sub> serves as the active cathode material.<sup>[2]</sup> In contrast to the 1.5 V class primary batteries, such as alkaline batteries<sup>[3]</sup> and metal–air batteries,<sup>[4]</sup> the nominal voltage of the Li-SO<sub>2</sub> battery is 3.0 V. Furthermore, the Li-SO<sub>2</sub> battery has an energy density of up to 330 Wh kg<sup>-1</sup>, which is 2–4 times greater than that of alkaline batteries. The unique characteristics of Li-SO<sub>2</sub> batteries has opened up some special applications beyond the capability of traditional primary

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batteries; heretofore, it has been widely used in military, industrial, and consumer applications requiring long service life.<sup>[2]</sup>

Despite these favorable attributes, the safety of the Li-SO<sub>2</sub> system limits its application.<sup>[2a,5]</sup> First, liquefied SO<sub>2</sub> is accumulated in the cell by pressure that necessitates that the cells can withstand pressures greater than 3.4 atm at 294 K without leaking toxic SO<sub>2</sub>. Furthermore, volatile acetonitrile is used as the electrolyte solvent, resulting in an uncontrolled increase in pressure, and the risk of fire, under abuse conditions. To overcome this limitation, numerous groups have investigated polar aprotic solvents, such as propylene carbonate, dimethoxyethane, and diglyme,<sup>[5a,c]</sup> as well as salts such as lithium tetrachloroaluminate<sup>[6]</sup> to reduce the reactivity and the vapor pressure of the electrolytes, but the former were flammable solvents and the latter were sensitive to moisture.

Herein, we have developed a novel ambient  $\text{Li-SO}_2$  battery using a functional ionic liquid (IL) as an electrolyte (Figure 1). This strategy involves optimizing the IL chemistry



Figure 1. Representation of the ambient IL-based Li-SO<sub>2</sub> battery.

to capture  $SO_2$  through reversible chemical absorption with basic ILs, while still maintaining the electrochemical activity of  $SO_2$ . This kind of new IL-SO<sub>2</sub> electrolyte materials exhibit extremely high conductivity, low viscosity, and high  $SO_2$  loading, which guarantees a high energy density and good discharge performance of the Li-SO<sub>2</sub> battery.

ILs are uniquely qualified for this application because of their physical properties. Specifically, they have near negligible vapor pressures, are nonflammable, and have wide electrochemical windows.<sup>[7]</sup> Owing to these attributes, ILs have been studied as electrolyte materials for various electrochemical devices, such as electrochemical capacitors,<sup>[8]</sup> lithium-ion batteries,<sup>[9]</sup> Li-O<sub>2</sub> and Li-S batteries,<sup>[10]</sup> but not Li-SO<sub>2</sub>

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batteries. The structure and properties of the IL can be finely adjusted by changing the cation or anion of the IL, and specific functionality can be introduced to the IL. In this context, a number of functional ILs have been reported to absorb  $SO_2$ , including guanidinium-based ILs,<sup>[11]</sup> azole-based ILs,<sup>[12]</sup> ether-functionalized ILs,<sup>[13]</sup> and several other anion-functionalized ILs,<sup>[14]</sup>

It is these characteristics that we have exploited and tailored in preparing the intrinsically stable Li-SO<sub>2</sub> batteries. In the following, we show how a high SO<sub>2</sub> loading and good discharge performance can be achieved by tuning the interaction between the ILs and SO<sub>2</sub>.

Four ILs having a different cation, anion, and functional groups were prepared, and their feasibility as electrolyte materials in the Li-SO<sub>2</sub> battery was explored. These ILs including three 1-alkyl-3-methylimidazolium-based ILs with different anions (SCN<sup>-</sup>, Cl<sup>-</sup>, and TFSI<sup>-</sup>) that possess tunable interaction sites and strength with SO<sub>2</sub>, and another IL with a piperdinium cation (Scheme 1). As the capacity of the Li-SO<sub>2</sub> battery is mainly dependent on the amount of SO<sub>2</sub> in the electrolyte, it is crucial for the ILs to capture as much SO<sub>2</sub> as possible under ambient conditions. Indeed, as listed in Table 1, [Bmim][SCN] shows excellent absorption capacity,



Scheme 1. Structures of the ILs in this work.

**Table 1:** SO<sub>2</sub> loading in ILs (q, mol SO<sub>2</sub> per mol IL) and conductivities ( $\sigma$ , mS cm<sup>-1</sup>) of ILs and IL-SO<sub>2</sub> composites with different SO<sub>2</sub> loading at 296.3 K.

	ILs		ILs with low SO <sub>2</sub> loading		SO <sub>2</sub> -saturated ILs <sup>[a]</sup>		
	σ	σ	9	σ	9	σ	σ
[Bmim][SCN]	4.4	3.3 <sup>[b]</sup>	0.59	16.1	2.91	68.1	41.6 <sup>[b]</sup>
[Emim][Cl]	_[c]	_[c]	0.62	13.8	2.75	90.1	78.4 <sup>[d]</sup>
[Bmim][TFSI]	3.9	2.6 <sup>[b]</sup>	0.67	9.5	1.33	17.3	10.3 <sup>[b]</sup>
[Bmpp][TFSI]	1.2	0.6 <sup>[b]</sup>	0.63	4.5	1.31	9.0	5.3 <sup>[b]</sup>

<sup>[</sup>a] The ILs were saturated at a SO<sub>2</sub> pressure of 1 bar and 296.3 K. [b] The ILs contain 0.5  $\mu$  LiTFSI. [c] [Emim]Cl is solid at 296.3 K. [d] The IL contain 0.3  $\mu$  LiTFSI.

and it can capture 2.91 mol SO<sub>2</sub> per mol IL through multiplesite interactions under ambient conditions (see below for a detailed absorption mechanism), that constitutes about 50% of the electrolyte weight. For comparison, in conventional organic-solvent-based Li-SO<sub>2</sub> cells, SO<sub>2</sub> constitutes about 70% of the electrolyte weight; however, the SO<sub>2</sub> pressure can reach as high as 3.4 atm at 294 K.<sup>[2]</sup> Furthermore, the temperature has a significant effect on the capacity of ILs. As the temperature increases from 286.1 to 316.1 K, the capacity of [Bmim][SCN] decreases from 3.52 to 1.85 mol mol<sup>-1</sup> (Supporting Information, Figure S1).

IL-SO<sub>2</sub> electrolytes also show extremely high conductivity. As shown in Table 1, the presence of SO<sub>2</sub> causes an increase in ionic conductivities of all of the IL-based electrolytes with or without lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), while their viscosities decrease significantly (Supporting Information, Table S1). For example, the conductivity of [Bmim][SCN]-SO<sub>2</sub> electrolytes with a SO<sub>2</sub> molar fraction of 0.59 is 16.1 mS cm<sup>-1</sup>, which is 3.6 times larger than that of pure [Bmim][SCN]. And the conductivity of SO<sub>2</sub>saturated [Bmim][SCN] electrolyte increases to a high value of 68 mS cm<sup>-1</sup> at ambient temperature and pressure, which is 15.4 times larger than that of pure [Bmim][SCN]. The conductivity of SO<sub>2</sub>-saturated [Emim][Cl] electrolyte even reaches 90.1 mS cm<sup>-1</sup>, which is comparable to that of aqueous electrolytes.<sup>[15]</sup> Similarly, the viscosity of SO<sub>2</sub>-saturated [bmim][SCN] electrolyte decrease to 6.8 mPas, which is far below that of pure IL (54.7 mPas). It is known that when aprotic ILs are used as electrolytes, the relatively high viscosity and the low conductivity caused by the intrinsic strong electrostatic interaction between ions are the main drawbacks for ILs.<sup>[7d,9a,c]</sup> Therefore, such high conductivities and low viscosities make the IL-SO<sub>2</sub> composites be attractive electrolyte materials for battery applications.

The ambient Li-SO<sub>2</sub> battery with ILs/LiTFSI as electrolytes was assembled in a glove box under an argon atmosphere (see the Supporting Information). A commercial carbon cloth with a pore volume of  $0.49 \text{ cm}^3 \text{g}^{-1}$  was used as the current collector for the cathode. Figure 2a shows the discharge performance of the Li-SO<sub>2</sub> batteries with SO<sub>2</sub>-saturated ILs as the electrolytes under a current rate of 20  $\mu$ A cm<sup>-2</sup>. These IL-based Li-SO<sub>2</sub> batteries have high working cell voltage above 2.7 V and characteristic flat



**Figure 2.** a) Discharge curves of ambient IL-based Li-SO<sub>2</sub> batteries with different ILs as electrolyte materials under a constant current density of 20  $\mu$ A cm<sup>-2</sup> at 296.3 K. b), c) EIS of IL-SO<sub>2</sub> batteries with different ILs after 24 h discharge at a constant current density of 20  $\mu$ A cm<sup>-2</sup>: b) [Bmim][SCN] and [Emim][CI], c) [Bmim][TFSI] and [Bmpp] [TFSI].

discharge curve, which are same as that of standard Li-SO<sub>2</sub> battery using an acetonitrile-based electrolyte.<sup>[2]</sup> This ambient Li-SO<sub>2</sub> battery also demonstrated a good continuous discharge performance for at least over 20 days (Supporting Information, Figure S2), and about 90% of solvated SO<sub>2</sub> still remained in the [Bmim][SCN]-based electrolyte after 20 days discharge. The open-circuit voltage of the Li-SO<sub>2</sub> batteries with IL electrolytes is  $3.0 \pm 0.5$  V, indicating that SO<sub>2</sub> is the active cathode material. Figure 2 a also shows the effect of the structure of the ILs on the discharge performance of the Li-SO<sub>2</sub> batteries. Different kind of anions investigated in this work had a slight effect on the discharge voltage, and the cell with [Bmim][SCN] as electrolyze has the highest discharge voltage of 2.83 V. When the cation is changed from 1-butyl-3methylimidazolium to N-butyl-N-methylpiperdinium, the discharge voltage of the IL-SO<sub>2</sub> battery with TFSI<sup>-</sup> anion decreases from 2.80 to 2.71 V.

Figure 2b and c show the electrical impedance spectroscopy (EIS) results of the four IL-based Li-SO<sub>2</sub> cells after 24 h discharge at a constant current density of  $20 \,\mu\text{A}\,\text{cm}^{-2}$ . The intercept at high frequency indicates the bulk resistance that mainly relates to the electrical conductivity of electrolyte and electrodes, and the strongly superimposed semicircle at high and medium frequencies is usually assigned to the solidelectrolyte interface resistance and charge-transfer resistance.<sup>[10b, 16]</sup> As shown in Figure 2b and c, it is clear that the cells with [Bmim][SCN] and [Bmim][Cl] as the electrolytes have a relatively small intercept at high frequency, which is consistent with the ionic conductivity data shown in Table 1. The semicircle radii of the [Bmim][SCN]-based cell is obviously smaller than those of other IL-based cells, indicating faster charge-transfer kinetics and a better discharge performance in the [bmim][SCN]-based cell.

The interactions between ILs and SO<sub>2</sub> were analyzed with ab initio calculations at the B3LYP/6-31 ++ G(d,p) level.<sup>[17]</sup> The minimum energy structures of the complexes with different ratios of IL and SO<sub>2</sub> are shown in Figure 3b,c, and in the Supporting Information, Figures S5-S7. The cation of [Bmim][SCN] was omitted for clarity in Figure 3b and c. As seen in these figures, the anions are the main sites to capture SO<sub>2</sub>. The calculated absorption enthalpies of SO<sub>2</sub> for [Bmim]-[TFSI]-SO<sub>2</sub> was -17.9 kJ mol<sup>-1</sup>, indicating it was a physical absorption. As for [Emim][Cl], the SO<sub>2</sub> uptake at 1 bar was 2.75 mol per mol of IL, and the absorption enthalpies of  $SO_2$ for [Emim][Cl]-SO<sub>2</sub> and [Emim][Cl]-2SO<sub>2</sub> complexes were  $-64.7 \text{ kJ} \text{mol}^{-1}$  and  $-49.0 \text{ kJ} \text{mol}^{-1}$ , respectively. Thus one mol of SO<sub>2</sub> was trapped in [Emim][Cl] by chemical absorption (absorption enthalpy  $< -50 \text{ kJ mol}^{-1}$ ). This chemical absorption mechanism was confirmed by a single-crystal X-ray diffraction experiment.<sup>[18]</sup>

In the case of [Bmim][SCN], almost 3 mol of SO<sub>2</sub> were captured by the IL through multiple-site interactions (Figure 3b, and Supporting Information, Figures S7). The absorption enthalpies of SO<sub>2</sub> for the [Bmim][SCN]-3SO<sub>2</sub>, [Bmim]-[SCN]-2SO<sub>2</sub>, and [Bmim][SCN]-SO<sub>2</sub> complexes were -35.4 kJ mol<sup>-1</sup>, -44.1 kJ mol<sup>-1</sup>, and -58.6 kJ mol<sup>-1</sup>, respectively. According to the calculated results, the interaction of SO<sub>2</sub> and IL in [Bmim][SCN]-SO<sub>2</sub> is mainly a chemical interaction; however, the interaction in [Bmim][SCN]-3SO<sub>2</sub>.



**Figure 3.** a) Discharge curves of an ambient [Bmim][SCN]-based Li-SO<sub>2</sub> battery with different SO<sub>2</sub> loadings under constant current density of 20  $\mu$ A cm<sup>-2</sup> and at 296.3 K; red curve: SO<sub>2</sub>-saturated [Bmim][SCN]; blue curve: [Bmim][SCN]-0.69SO<sub>2</sub>. Insets: the interaction and the enthalpy of [Bmim]SCN-3SO<sub>2</sub> (b) and [Bmim]SCN-SO<sub>2</sub> (c); O red, S yellow, N blue, C gray. d) Discharge voltages of an ambient [Bmim]-[SCN]-based Li-SO<sub>2</sub> battery under different current densities at 296.3 K.

is in the physical regime. Thus, during the discharge process accompanied with  $SO_2$  desorption, the interaction between the  $SO_2$  and [Bmim][SCN] changes gradually from a physical interaction to a chemical interaction because of the increase in absorption enthalpy.

It is thus an important issue whether all of SO<sub>2</sub> captured by ILs through chemical and physical absorption are available for electrochemical reduction reaction. In this work, the discharge performance of Li-SO<sub>2</sub> batteries with [Bmim]-[SCN]-0.69 SO<sub>2</sub> and [Bmim][TFSI]-0.64 SO<sub>2</sub> as electrolytes, respectively, were evaluated and the results were compared with that of SO<sub>2</sub>-saturated cells. As shown in Figure 3a, the [Bmim][SCN]-0.69 SO<sub>2</sub> cell also shows characteristic flat discharge curves, although the working voltage is slightly below that of SO<sub>2</sub>-saturated [bmim][SCN], revealing that all of the SO<sub>2</sub>, regardless of chemical absorption or physical absorption, are capable of discharging. Similar discharge behavior was observed in the [Bmim][TFSI]-0.64 SO<sub>2</sub> cell (Supporting Information, Figure S3). Therefore, with [Bmim][SCN] as an example, the aforementioned studies clearly show that it is a practical approach to simultaneously achieve high SO<sub>2</sub> loading and satisfactory discharge performance in a Li-SO<sub>2</sub> battery using an IL electrolyte with multiple-site SO<sub>2</sub> interactions.

The ambient Li-SO<sub>2</sub> batteries based on IL electrolytes not only have good discharge performance but also have good rate capability. The working voltage of the Li-SO<sub>2</sub> batteries with [Bmim][SCN] (Figure 3d) and [Bmim][TFSI] (Support-



ing Information, Figure S4) as the electrolytes decreased slightly with the increase of discharge current density. For example, the working voltage in the [Bmim][SCN]-SO<sub>2</sub> cell decreases from 2.83 to 2.74 V as the current density increases from 38 to 159  $\mu$ m cm<sup>-2</sup>.

The cathode discharge products were examined with infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Figure 4a shows the IR spectra of the cathode products from the Li-SO<sub>2</sub> cell with [Bmim][TFSI]



**Figure 4.** a) IR spectra of the cathode product from an ambient IL-SO<sub>2</sub> battery discharged under constant current density of 20  $\mu$ A cm<sup>-2</sup> for 30 days at 296.3 K. b) High-resolution S2p XPS spectrum of the cathode discharge product along with a computer fitted curve of this spectrum.

as the electrolyte that discharged at 296.3 K for 10 days. The strong IR peaks at 1080, 1015, and 896 cm<sup>-1</sup> are attributed to the absorption of dithionite  $(Li_2S_2O_4)$ ,<sup>[19]</sup> indicating that the main component of the discharge product was Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Furthermore, three moderate peaks at 1248, 1166, and 954 cm<sup>-1</sup> appeared in Figure 4a; the first two peaks were assigned to polythionates  $Li_2S_nO_6$  (n > 3) and the peak of 954 cm<sup>-1</sup> belongs to the O-S stretching of sulfite SO<sub>3</sub>.<sup>[19]</sup> Figure 4b shows a high-resolution S2p XPS spectrum of the cathode discharge product along with computer-fitted curves of the spectrum. It appears that at least three different S oxidation states are present. According to the reference data,<sup>[20]</sup> the binding energy at 166.5 eV was assigned to  $Li_2S_2O_4$ , while those at 162.7 and 168.7 eV were assigned to - $S^+$  and  $-SO_3^{2-}$  sulfur 2p in Li<sub>2</sub>S<sub>0</sub>O<sub>6</sub> and Li<sub>2</sub>SO<sub>3</sub>, respectively. Based on both IR and XPS results, the principal discharge product from the IL-based Li-SO<sub>2</sub> cell was Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Figure 1), with other minor compounds such as  $Li_2SO_3$  and  $Li_2S_nO_6$ . These minor compounds probably result from the instability of Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> under ambient conditions, which will decompose to sulfite and sulfur.[20]

In summary, we have developed an ambient Li-SO<sub>2</sub> battery by capturing SO<sub>2</sub> in the cell through reversible chemical absorption and strong physical absorption with functional ILs as the electrolytes. Our work shows that both

chemically and physically captured  $SO_2$  with absorption enthalpy less than -64.7 kJ mol<sup>-1</sup> have good electrochemical activity during discharge. Furthermore, a high energy density and good discharge performance with working voltage over 2.8 V was achieved using an IL electrolyte with multiple-site  $SO_2$  interactions. This strategy based on reversible chemical absorption of  $SO_2$  in IL-electrolytes opens a new avenue to improve the safety of Li-SO<sub>2</sub> batteries and is also helpful for the development of next generation of ambient Li-SO<sub>2</sub> batteries.

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