DOI: 10.1002/ange.201309539

Lithium Batteries **Hot Paper**

Ambient Lithium–SO_2 Batteries with Ionic Liquids as Electrolytes**

Huabin Xing,* Chen Liao, Qiwei Yang, Gabriel M. Veith, Bingkun Guo, Xiao-Guang Sun,*
Qilong Ren, Yong-Sheng Hu, and Sheng Dai*

Abstract: *Li-SO_2 batteries have a high energy density but bear serious safety problems that are associated with pressurized SO_2 and flammable solvents in the system. Herein, a novel ambient Li-SO_2 battery was developed through the introduction of ionic liquid (IL) electrolytes with tailored basicities to solvate SO_2 by reversible chemical absorption. By tuning the interactions of ILs with SO_2, 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_2 in IL electrolytes enables the development of the next generation of ambient Li-SO_2 batteries.*

Energy storage is of central importance for modern society.[1] The lithium–sulfur dioxide (Li-SO_2) battery is a lightweight, long-life, high energy density primary battery in which cheap, abundant SO_2 serves as the active cathode material.[2] In contrast to the 1.5 V class primary batteries, such as alkaline batteries[3] and metal–air batteries,[4] the nominal voltage of the Li-SO_2 battery is 3.0 V. Furthermore, the Li-SO_2 battery has an energy density of up to 330 Wh kg^{-1}, which is 2–4 times greater than that of alkaline batteries. The unique characteristics of Li-SO_2 batteries has opened up some special applications beyond the capability of traditional primary batteries; heretofore, it has been widely used in military, industrial, and consumer applications requiring long service life.[2]

Despite these favorable attributes, the safety of the Li-SO_2 system limits its application.[2a,5] First, liquefied SO_2 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_2. 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,[5a,c] as well as salts such as lithium tetrachloroaluminate[6] 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 Li-SO_2 battery using a functional ionic liquid (IL) as an electrolyte (Figure 1). This strategy involves optimizing the IL chemistry 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_2 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_2 battery.

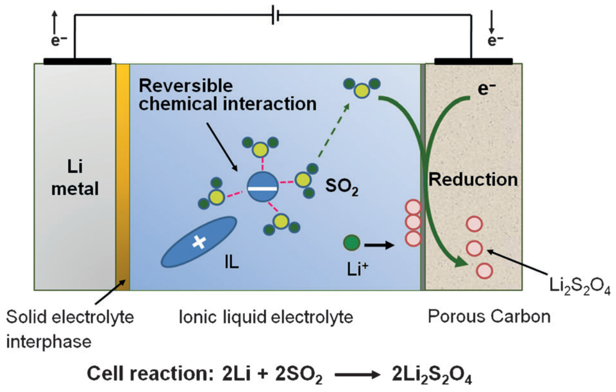


Figure 1. Representation of the ambient IL-based Li-SO_2 battery.

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.[7] Owing to these attributes, ILs have been studied as electrolyte materials for various electrochemical devices, such as electrochemical capacitors,[8] lithium-ion batteries,[9] Li-O_2 and Li-S batteries,[10] but not Li-SO_2

---

[*] Dr. H. B. Xing, Dr. Q. W. Yang, Prof. Q. L. Ren
Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemical and Biological Engineering, Zhejiang University
Hangzhou 310027 (China)
E-mail: xinghb@zju.edu.cn

Dr. H. B. Xing, Dr. C. Liao, Dr. B. K. Guo, Dr. X. G. Sun, Prof. S. Dai
Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)
E-mail: sunx@ornl.gov
dais@ornl.gov

Dr. G. M. Veith
Materials Science and Technology Division
Oak Ridge National Laboratory, Oak Ridge, TN 37831 (USA)

Prof. S. Dai
Department of Chemistry, University of Tennessee
Knoxville, TN 37966 (USA)

Prof. Y. S. Hu
National Laboratory for Condensed Matter Physics
Institute of Physics, Chinese Academy of Sciences
Beijing, 100190 (China)

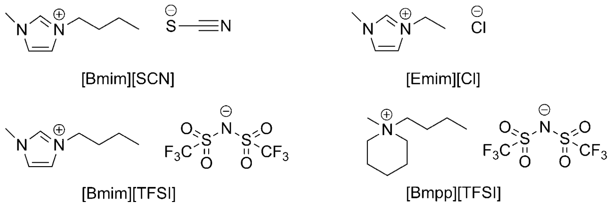
[**] The experimental part of this research was supported by the U.S. Department of Energy's Office of Basic Energy Science, Division of Materials Sciences and Engineering; the calculation was supported by National Natural Science Foundation of China (21222601, 20936005), and the Zhejiang Provincial Natural Science Foundation of China (LR13B060001).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309539.

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,[11] azole-based ILs,[12] ether-functionalized ILs,[13] and several other anion-functionalized ILs.[14]

It is these characteristics that we have exploited and tailored in preparing the intrinsically stable Li-SO_2 batteries. In the following, we show how a high SO_2 loading and good discharge performance can be achieved by tuning the interaction between the ILs and SO_2.

Four ILs having a different cation, anion, and functional groups were prepared, and their feasibility as electrolyte materials in the Li-SO_2 battery was explored. These ILs including three 1-alkyl-3-methylimidazolium-based ILs with different anions (SCN^-, Cl^-, and $TFSI^-$) that possess tunable interaction sites and strength with SO_2, and another IL with a piperdinium cation (Scheme 1). As the capacity of the Li-SO_2 battery is mainly dependent on the amount of SO_2 in the electrolyte, it is crucial for the ILs to capture as much SO_2 as possible under ambient conditions. Indeed, as listed in Table 1, [Bmim][SCN] shows excellent absorption capacity, and it can capture 2.91 mol SO_2 per mol IL through multiple-site 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_2 cells, SO_2 constitutes about 70% of the electrolyte weight; however, the SO_2 pressure can reach as high as 3.4 atm at 294 K.[2] 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^{-1} (Supporting Information, Figure S1).



Scheme 1. Structures of the ILs in this work.

Table 1: SO_2 loading in ILs (q, mol SO_2 per mol IL) and conductivities (σ, mS cm^{-1}) of ILs and IL-SO_2 composites with different SO_2 loading at 296.3 K.

	ILs		ILs with low SO_2 loading		SO_2-saturated ILs[a]		
	σ	σ	q	σ	q	σ	σ
[Bmim][SCN]	4.4	3.3[b]	0.59	16.1	2.91	68.1	41.6[b]
[Emim][Cl]	–[c]	–[c]	0.62	13.8	2.75	90.1	78.4[d]
[Bmim][TFSI]	3.9	2.6[b]	0.67	9.5	1.33	17.3	10.3[b]
[Bmpp][TFSI]	1.2	0.6[b]	0.63	4.5	1.31	9.0	5.3[b]

[a] The ILs were saturated at a SO_2 pressure of 1 bar and 296.3 K. [b] The ILs contain 0.5 M LiTFSI. [c] [Emim]Cl is solid at 296.3 K. [d] The IL contain 0.3 M LiTFSI.

IL-SO_2 electrolytes also show extremely high conductivity. As shown in Table 1, the presence of SO_2 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_2 electrolytes with a SO_2 molar fraction of 0.59 is 16.1 mS cm^{-1}, which is 3.6 times larger than that of pure [Bmim][SCN]. And the conductivity of SO_2-saturated [Bmim][SCN] electrolyte increases to a high value of 68 mS cm^{-1} at ambient temperature and pressure, which is 15.4 times larger than that of pure [Bmim][SCN]. The conductivity of SO_2-saturated [Emim][Cl] electrolyte even reaches 90.1 mS cm^{-1}, which is comparable to that of aqueous electrolytes.[15] Similarly, the viscosity of SO_2-saturated [bmim][SCN] electrolyte decrease to 6.8 mPa s, which is far below that of pure IL (54.7 mPa s). 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.[7d, 9a,c] Therefore, such high conductivities and low viscosities make the IL-SO_2 composites be attractive electrolyte materials for battery applications.

The ambient Li-SO_2 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 cm^3 g^{-1} was used as the current collector for the cathode. Figure 2a shows the discharge performance of the Li-SO_2 batteries with SO_2-saturated ILs as the electrolytes under a current rate of 20 μA cm^{-2}. These IL-based Li-SO_2 batteries have high working cell voltage above 2.7 V and characteristic flat

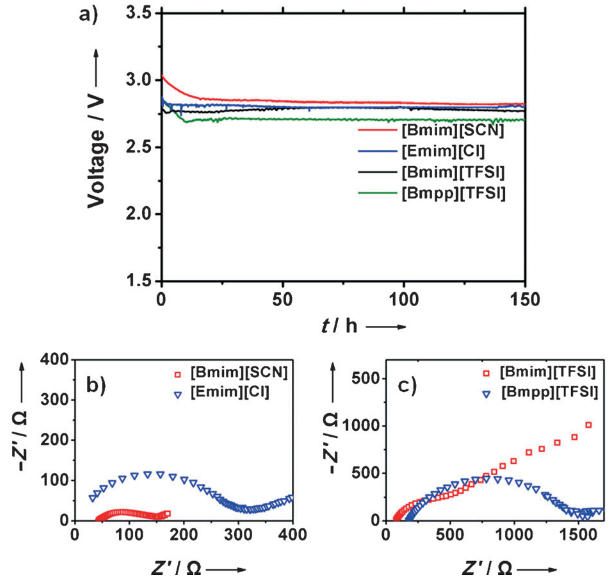


Figure 2. a) Discharge curves of ambient IL-based Li-SO_2 batteries with different ILs as electrolyte materials under a constant current density of 20 μA cm^{-2} at 296.3 K. b), c) EIS of IL-SO_2 batteries with different ILs after 24 h discharge at a constant density of 20 μA cm^{-2}: b) [Bmim][SCN] and [Emim][Cl], c) [Bmim][TFSI] and [Bmpp] [TFSI].

discharge curve, which are same as that of standard Li-SO_2 battery using an acetonitrile-based electrolyte.[2] This ambient Li-SO_2 battery also demonstrated a good continuous discharge performance for at least over 20 days (Supporting Information, Figure S2), and about 90% of solvated SO_2 still remained in the [Bmim][SCN]-based electrolyte after 20 days discharge. The open-circuit voltage of the Li-SO_2 batteries with IL electrolytes is 3.0 ± 0.5 V, indicating that SO_2 is the active cathode material. Figure 2a also shows the effect of the structure of the ILs on the discharge performance of the Li-SO_2 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-3-methylimidazolium to *N*-butyl-*N*-methylpiperdinium, the discharge voltage of the IL-SO_2 battery with $TFSI^-$ 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_2 cells after 24 h discharge at a constant current density of $20\,\mu A\,cm^{-2}$. 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 solid-electrolyte interface resistance and charge-transfer resistance.[10b,16] 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_2 were analyzed with ab initio calculations at the B3LYP/6-31++G(d,p) level.[17] The minimum energy structures of the complexes with different ratios of IL and SO_2 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_2. The calculated absorption enthalpies of SO_2 for [Bmim]-[TFSI]-SO_2 was $-17.9\,kJ\,mol^{-1}$, indicating it was a physical absorption. As for [Emim][Cl], the SO_2 uptake at 1 bar was 2.75 mol per mol of IL, and the absorption enthalpies of SO_2 for [Emim][Cl]-SO_2 and [Emim][Cl]-2SO_2 complexes were $-64.7\,kJ\,mol^{-1}$ and $-49.0\,kJ\,mol^{-1}$, respectively. Thus one mol of SO_2 was trapped in [Emim][Cl] by chemical absorption (absorption enthalpy $< -50\,kJ\,mol^{-1}$). This chemical absorption mechanism was confirmed by a single-crystal X-ray diffraction experiment.[18]

In the case of [Bmim][SCN], almost 3 mol of SO_2 were captured by the IL through multiple-site interactions (Figure 3b, and Supporting Information, Figures S7). The absorption enthalpies of SO_2 for the [Bmim][SCN]-3SO_2, [Bmim]-[SCN]-2SO_2, and [Bmim][SCN]-SO_2 complexes were $-35.4\,kJ\,mol^{-1}$, $-44.1\,kJ\,mol^{-1}$, and $-58.6\,kJ\,mol^{-1}$, respectively. According to the calculated results, the interaction of SO_2 and IL in [Bmim][SCN]-SO_2 is mainly a chemical interaction; however, the interaction in [Bmim][SCN]-3SO_2 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.

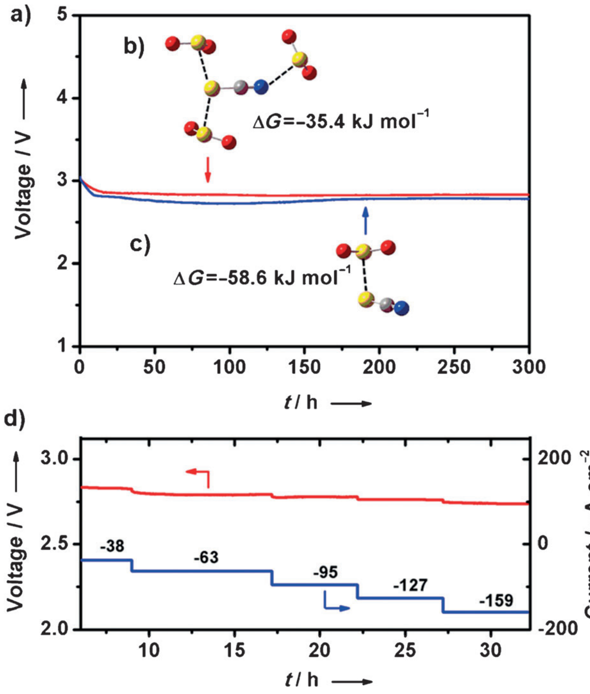


Figure 3. a) Discharge curves of an ambient [Bmim][SCN]-based Li-SO_2 battery with different SO_2 loadings under constant current density of $20\,\mu A\,cm^{-2}$ and at 296.3 K; red curve: SO_2-saturated [Bmim][SCN]; blue curve: [Bmim][SCN]-0.69SO_2. Insets: the interaction and the enthalpy of [Bmim]SCN-3SO_2 (b) and [Bmim]SCN-SO_2 (c); O red, S yellow, N blue, C gray. d) Discharge voltages of an ambient [Bmim]-[SCN]-based Li-SO_2 battery under different current densities at 296.3 K.

It is thus an important issue whether all of SO_2 captured by ILs through chemical and physical absorption are available for electrochemical reduction reaction. In this work, the discharge performance of Li-SO_2 batteries with [Bmim]-[SCN]-0.69SO_2 and [Bmim][TFSI]-0.64SO_2 as electrolytes, respectively, were evaluated and the results were compared with that of SO_2-saturated cells. As shown in Figure 3a, the [Bmim][SCN]-0.69SO_2 cell also shows characteristic flat discharge curves, although the working voltage is slightly below that of SO_2-saturated [bmim][SCN], revealing that all of the SO_2, regardless of chemical absorption or physical absorption, are capable of discharging. Similar discharge behavior was observed in the [Bmim][TFSI]-0.64SO_2 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_2 loading and satisfactory discharge performance in a Li-SO_2 battery using an IL electrolyte with multiple-site SO_2 interactions.

The ambient Li-SO_2 batteries based on IL electrolytes not only have good discharge performance but also have good rate capability. The working voltage of the Li-SO_2 batteries with [Bmim][SCN] (Figure 3d) and [Bmim][TFSI] (Supporting 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_2 cell decreases from 2.83 to 2.74 V as the current density increases from 38 to 159 $\mu m\,cm^{-2}$.

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_2 cell with [Bmim][TFSI] as the electrolyte that discharged at 296.3 K for 10 days. The strong IR peaks at 1080, 1015, and 896 cm^{-1} are attributed to the absorption of dithionite ($Li_2S_2O_4$),[19] indicating that the main component of the discharge product was $Li_2S_2O_4$. Furthermore, three moderate peaks at 1248, 1166, and 954 cm^{-1} appeared in Figure 4a; the first two peaks were assigned to polythionates $Li_2S_nO_6$ ($n > 3$) and the peak of 954 cm^{-1} belongs to the O−S stretching of sulfite SO_3.[19] Figure 4b shows a high-resolution S 2p 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,[20] 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 $Li_2S_nO_6$ and Li_2SO_3, respectively. Based on both IR and XPS results, the principal discharge product from the IL-based Li-SO_2 cell was $Li_2S_2O_4$ (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 $Li_2S_2O_4$ under ambient conditions, which will decompose to sulfite and sulfur.[20]

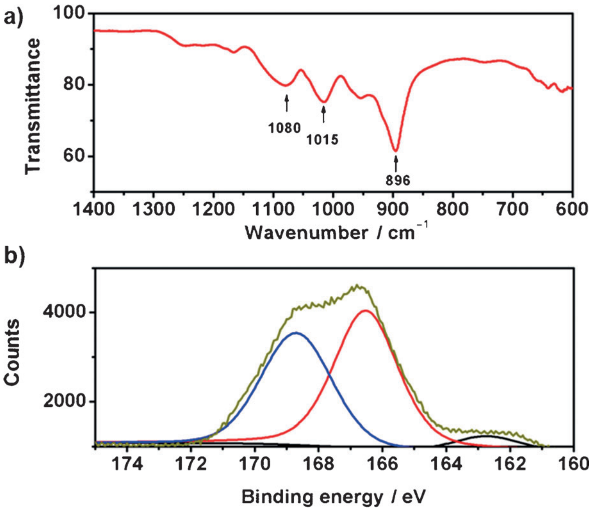


Figure 4. a) IR spectra of the cathode product from an ambient IL-SO_2 battery discharged under constant current density of 20 $\mu A\,cm^{-2}$ for 30 days at 296.3 K. b) High-resolution S 2p XPS spectrum of the cathode discharge product along with a computer fitted curve of this spectrum.

In summary, we have developed an ambient Li-SO_2 battery by capturing SO_2 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^{-1} 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_2 batteries and is also helpful for the development of next generation of ambient Li-SO_2 batteries.

Received: November 2, 2013

Keywords: absorption · ionic liquids · lithium · primary batteries · sulfur dioxide

[1] a) P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.* **2012**, *11*, 19–29; b) J. B. Goodenough, K. S. Park, *J. Am. Chem. Soc.* **2013**, *135*, 1167–1176; c) M. Armand, J. M. Tarascon, *Nature* **2008**, *451*, 652–657; d) P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew. Chem.* **2008**, *120*, 2972–2989; *Angew. Chem. Int. Ed.* **2008**, *47*, 2930–2946; e) A. Manthiram, Y. Z. Fu, Y. S. Su, *J. Phys. Chem. Lett.* **2013**, *4*, 1295–1297.

[2] a) B. V. Ratnakumar, M. C. Smart, R. C. Ewell, L. D. Whitcanack, A. Kindler, S. R. Narayanan, S. Surampudi, *J. Electrochem. Soc.* **2007**, *154*, A715–A724; b) G. T. K. Fey, *J. Power Sources* **1991**, *35*, 153–162; c) D. Linden, B. Macdonald, *J. Power Sources* **1980**, *5*, 35–55; d) H. F. Bittner, *J. Electrochem. Soc.* **1989**, *136*, 3147–3152.

[3] a) Y. Paik, J. P. Osegovic, F. Wang, W. Bowden, C. P. Grey, *J. Am. Chem. Soc.* **2001**, *123*, 9367–9377; b) F. Y. Cheng, J. Chen, *Chem. Soc. Rev.* **2012**, *41*, 2172–2192.

[4] a) Y. Li, M. Gong, Y. Y. Liang, J. Feng, J. E. Kim, H. L. Wang, G. S. Hong, B. Zhang, H. J. Dai, *Nat. Commun.* **2013**, *4*, 1805; b) H. Zhang, X. Zhong, J. C. Shaw, L. Liu, Y. Huang, X. Duan, *Energy Environ. Sci.* **2013**, *6*, 2621–2625.

[5] a) W. P. Kilroy, W. Ebner, D. L. Chua, H. V. Venkatasetty, *J. Electrochem. Soc.* **1985**, *132*, 274–281; b) W. P. Kilroy, *J. Electrochem. Soc.* **1985**, *132*, 998–1005; c) A. N. Dey, *J. Electrochem. Soc.* **1980**, *127*, 1886–1890.

[6] a) A. N. Dey, W. L. Bowden, H. C. Kuo, M. L. Gopikanth, C. Schlaikjer, D. Foster, *J. Electrochem. Soc.* **1989**, *136*, 1618–1621; b) A. N. Dey, H. C. Kuo, P. Piliero, M. Kallianidis, *J. Electrochem. Soc.* **1988**, *135*, 2115–2120; c) C. W. Park, S. M. Oh, *J. Power Sources* **1997**, *68*, 338–343.

[7] a) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, *8*, 621–629; b) P. Barpanda, J. Chotard, C. Delacourt, M. Reynaud, Y. Filinchuk, M. Armand, M. Deschamps, J. Tarascon, *Angew. Chem.* **2011**, *123*, 2574–2579; *Angew. Chem. Int. Ed.* **2011**, *50*, 2526–2531; c) D. R. MacFarlane, M. Forsyth, C. P. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil, E. Izgorodina, *Acc. Chem. Res.* **2007**, *40*, 1165–1173; d) C. A. Angell, N. Byrne, J. P. Belieres, *Acc. Chem. Res.* **2007**, *40*, 1228–1236.

[8] P. Simon, Y. Gogotsi, *Nat. Mater.* **2008**, *7*, 845–854.

[9] a) S. S. Moganty, N. Jayaprakash, J. L. Nugent, J. Shen, L. A. Archer, *Angew. Chem.* **2010**, *122*, 9344–9347; *Angew. Chem. Int. Ed.* **2010**, *49*, 9158–9161; b) H. Matsumoto, H. Sakaebe, K. Tatsumi, *J. Power Sources* **2005**, *146*, 45–50; c) H. Yoon, G. H. Lane, Y. Shekibi, P. C. Howlett, M. Forsyth, A. S. Best, D. R. MacFarlane, *Energy Environ. Sci.* **2013**, *6*, 979–986.

[10] a) T. Zhang, H. S. Zhou, *Angew. Chem.* **2012**, *124*, 11224–11229; *Angew. Chem. Int. Ed.* **2012**, *51*, 11062–11067; b) X. G. Sun, X.

Wang, R. T. Mayes, S. Dai, *ChemSusChem* **2012**, *5*, 2079 – 2085; c) B. K. Guo, T. Ben, Z. H. Bi, G. M. Veith, X. G. Sun, S. L. Qiu, S. Dai, *Chem. Commun.* **2013**, *49*, 4905 – 4907; d) X. L. Ji, L. F. Nazar, *J. Mater. Chem.* **2010**, *20*, 9821 – 9826; e) L. M. Suo, Y. S. Hu, H. Li, M. Armand, L. Q. Chen, *Nat. Commun.* **2013**, *4*, 1481.

[11] a) W. Z. Wu, B. X. Han, H. X. Gao, Z. M. Liu, T. Jiang, J. Huang, *Angew. Chem.* **2004**, *116*, 2469 – 2471; *Angew. Chem. Int. Ed.* **2004**, *43*, 2415 – 2417; b) J. Huang, A. Riisager, P. Wasserscheid, R. Fehrmann, *Chem. Commun.* **2006**, 4027 – 4029.

[12] C. M. Wang, G. K. Cui, X. Y. Luo, Y. J. Xu, H. R. Li, S. Dai, *J. Am. Chem. Soc.* **2011**, *133*, 11916 – 19919.

[13] S. Y. Hong, J. Im, J. Palgunadi, S. D. Lee, J. S. Lee, H. S. Kim, M. Cheong, K. D. Jung, *Energy Environ. Sci.* **2011**, *4*, 1802 – 1806.

[14] a) M. B. Shiflett, A. Yokozeki, *Ind. Eng. Chem. Res.* **2010**, *49*, 1370 – 1377; b) R. A. Ando, L. J. A. Siqueira, F. C. Bazito, R. M. Torresi, P. S. Santos, *J. Phys. Chem. B* **2007**, *111*, 8717 – 8719; c) C. M. Wang, J. J. Zheng, G. K. Cui, X. Y. Luo, Y. Guo, H. R. Li, *Chem. Commun.* **2013**, *49*, 1166 – 1168; d) M. J. Monteiro, R. A. Ando, L. J. A. Siqueira, F. F. Camilo, P. S. Santos, M. C. C. Ribeiro, R. M. Torresi, *J. Phys. Chem. B* **2011**, *115*, 9662 – 9670.

[15] W. Xu, C. A. Angell, *Science* **2003**, *299-302*, 422 – 425.

[16] X. G. Sun, C. A. Angell, *Electrochem. Commun.* **2009**, *11*, 1418 – 1421.

[17] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[18] R. W. Berg, P. Harris, A. Riisager, R. Fehrmann, *J. Phys. Chem. A* **2013**, DOI: 10.1021/jp408069n.

[19] R. L. Ake, D. M. Oglesby, W. P. Kilroy, *J. Electrochem. Soc.* **1984**, *131*, 968 – 974.

[20] K. M. Abraham, S. M. Chaudhri, *J. Electrochem. Soc.* **1986**, *133*, 1307 – 1311.