RSC Advances




ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

COMMUNICATION

# Solvate ionic liquid electrolyte with 1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether as a support solvent for advanced lithium-sulfur batteries

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hai Lu,[*a] Yan Yuan,[b] Zhenzhong Hou,[a] Yanqing Lai,[c] Kai Zhang[c] and Yexiang Liu[c]

**1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether (TFTFE) was added to solvate ionic liquid (SIL) based on glyme-lithium salt as a support solvent. The fluorinated ether improves cycle and rate capability of Li-S cells. The key role of TFTFE played in the cell system with SIL is an ionic conduction-enhancing ingredient, especially for high-rate cycle environment.**

The issues of energy shortage and environment pollution propel the development of electric vehicles. To cater the strict requests for vehicle-loaded power, all kinds of advanced energy storage devices have been studied extensively.[1] Among these, lithium sulfur (Li-S) battery has attracted worldwide attentions by virtue of its theoretical energy density of up to 2600 Wh $kg^{-1}$,[2] which is 10 times higher than that of conventional lithium-ion batteries (LIB). Besides, sulfur has the advantages of non-toxicity and abundance in nature, whereas LIB cathode materials typically contain rare metals.

However, a critical problem originated from redox conversion process of the Li-S batteries is the dissolution of reaction intermediate polysulfides (PS) in the electrolyte.[3] The dissolved PS tends to generate repeating shuttle between the cathode and anode,[4] resulting in low coulombic efficiency and fast self-discharge. Furthermore, the PS can be electrochemically and chemically reduced on Li metal, causing such problems as (a) consuming active species, (b) corroding Li anode, and (c) polarizing Li anode once insoluble products are formed and deposited on the Li surface.[5] Hence the restrictions towards PS are very necessary for boosting cell performance. Optimizing electrolyte composition is often attempted for this purpose, e.g., altering solvent type, controlling electrolyte amount or introducing functional additives, etc.[6-8] However these approaches are still hard to avoid the dissolution and shuttle of PS completely.

Recently, solvate ionic liquid (SIL)[9] begins to enter the research scope of the Li-S batteries owing to its distinctive structure and properties. The typical case of SIL is the equimolar mixtures of tetraglyme (G4) and certain Li salts (LiX).[10] The formation of complex $Li(G4)_1X$ will weaken the donor ability of G4 solvent because all of the lone pairs of the ether oxygen atoms are donated to the $Li^+$ (as we know, the coordination number of $Li^+$ is 4~5).[11] Thus the PS is poorly solvated in the SIL and quite low solubility of PS can be obtained easily in SIL,[12] which reflects the superiority of SIL applying in the Li-S batteries compared to other electrolyte systems. Research results show that SIL electrolyte allow the cell to have a stable charge-discharge cycles and a coulombic efficiency of greater than 99%.[12] However, the cell capacity is still a bit low over the whole cycling period. Besides, the high viscosity of the SIL gives rise to certain polarization, which is harmful to the potential plateau and rate capability of the cell. Interestingly, It is reported that organo-fluorine compound is capable of enhancing the energy and power density once it was added into the SIL,[11] which utilizes the complementary and synergistic actions between SIL and fluorinated ether.

In the study, we aims to select another novel fluorinated ether derivative named 1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether (TFTFE) as the support solvent of SIL. Significant improvements of TFTFE-contained electrolyte on electrochemical performances of the Li-S cell are demonstrated here, and the key role of TFTFE in the cell system with SIL is discussed. Several electrolytes using in this experiment were prepared as follows: Lithium bis(trifluoromethane sulfonel)imide (LiTFSI, Aldrich) and G4 (Adamas) were mixed at equimolar ratio and magnetically stirred at 50 ºC overnight in a argon-filled glove box, forming $Li(G4)_1TFSI$ (LiTFSI:G4=1:1, molar ratio). Then the stoichiometric TFTFE (Adamas) was further added into above $Li(G4)_1TFSI$ to obtain a series of solution mixtures $Li(G4)_1TFSI$-xTF (LiTFSI:G4:TFTFE=1:1:x, molar ratio, x=1~6).

In general, the required properties of a support solvent for SIL electrolyte $Li(G4)_1TFSI$ in Li-S cells include:[11]

(a) Chemical stability against PS;
(b) Reductive stability against Li metal;
(c) Miscibility with $Li(G4)_1TFSI$;
(d) Better mobility than $Li(G4)_1TFSI$;

[a] School of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, China. Email: lhxust@126.com
[b] School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
[c] School of Metallurgy and Environment, Central South University, Changsha 410083, China

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

(e) Low donor ability for limiting PS dissolution;

(f) Weak interaction with solvate structure of $Li(G4)_1TFSI$.

We have exhibited for the first time that TFTFE is suitable for application in Li-S cells as a co-solvent.[13] Reversible capacity and coulombic efficiency of the cell can be increased distinctly when TFTFE was mixed with conventional ethers. So it is undoubted that TFTFE owns favourable chemical stability against PS and reductive stability against Li metal. Meanwhile, the fluorinated ether is miscible with conventional ethers such as G4, thus also can be blended with $Li(G4)_1TFSI$. As for the mobility, the conductivity meter (Mettler Toledo, SG3) and viscometer (Brookfield, DV2T-LV) were used for measuring the conductivity and viscosity of the electrolyte, respectively. It is found that $Li(G4)_1TFSI$-4TF has higher ion conductivity and lower viscosity (6.81 ms $cm^{-1}$ and 4.56 mPa s as measured) than $Li(G4)_1TFSI$ (1.6 ms $cm^{-1}$ and 81 mPa s as reported[10]), which means TFTFE favours the improvement of transport property on the basis of SIL.

The fluorinated ether has very low donor ability because it is always too fluorinated to participate in $Li^+$ solvation.[14] In order to realize the solubility of PS in various electrolytes, S and $Li_2S$ with a molar ratio of 7:1 were mixed and added in each electrolyte (the theoretical content of $Li_2S_8$ was controlled to be 0.25 mol $L^{-1}$). As the solubility of PS in the electrolyte has been characterized extensively by observing the colour of the electrolyte containing PS,[15,16] the pictures of various solutions after different standing time are recorded and compared in Fig.1a. Generally, the normal electrolyte without any PS presents colourless and transparent. However, the colour of $Li(G4)_1TFSI$ once adding $Li_2S_8$ becomes yellow and deepens gradually with time. In principle, the lone pairs of the ether oxygen are all donated to $Li^+$ in $Li(G4)_1TFSI$, and the stable $Li(G4)_1^+$ complex ion can be formed due to strong ion-dipole interaction between $Li^+$ and G4.[17] Hence PS dissolves hardly in the SIL. But the above colour change suggests that the solubility of PS still exists to some extent for $Li(G4)_1TFSI$. When using TFTFE as support solvent, the $Li(G4)_1TFSI$-xTF solution seems lighter than $Li(G4)_1TFSI$ at the same standing steps. Especially the colour of $Li(G4)_1TFSI$-4TF is close to colourless and nearly unchanged after standing for 6 days. It suggests that the dissolution of PS is further decreased in the TFTFE-contained electrolyte. Moreover, the dissolution quantity of polysulfide decreases gradually as TFTFE content in the electrolyte raises (see ESI, Fig.S1 and Fig.S2†). Therefore, more TFTFE contributes to weaker dissociation of PS compared to $Li(G4)_1TFSI$.

The low donor ability implies that TFTFE is hard to overwhelm G4 in $Li^+$ solvation as well. This speculation can be verified from linear sweep voltammetry (LSV) measurements of stainless steel/Li cells loaded various electrolytes (scanning rate: 0.5 mV $S^{-1}$). As shown in Fig.1b, the anodic limits of equimolar complex $Li(G4)_1TFSI$ is near 5 V vs. $Li/Li^+$, exhibiting high oxidative stability of the SILs. After adding TFTFE, the LSV curves of $Li(G4)_1TFSI$-xTF move towards low-potential direction slightly. The free ether (G4, in this case), which are not involved in the complex with $Li^+$, will be decomposed irreversibly at higher than 4 V vs. $Li/Li^+$.[18] The oxidative limits of $Li(G4)_1TFSI$-xTF is very close to that of $Li(G4)_1TFSI$, revealing that the majority of complex cations $Li(G4)_1^+$ still exist steadily and free G4 is scarce in the TFTFE-contained system. In other words, the

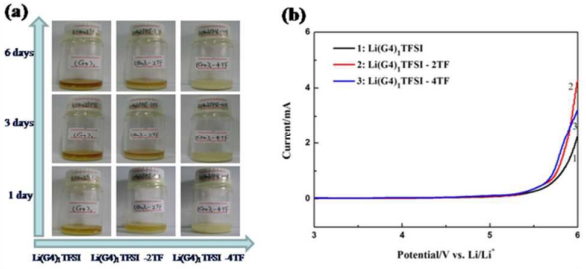


Fig.1 (a) solubility experiments of polysulfides in various electrolytes; (b) LSV measurements of various electrolytes at a scanning rate of 5 mV $s^{-1}$

distinctive solvate structure of SIL can be reserved although TFTFE was introduced into the electrolyte.

It can be seen from the above results that TFTFE meets all the demands for support solvent of SIL and can cooperate ideally with it. Next the electrochemical performances of Li-S cells with various electrolytes were investigated. Sulfur-carbon composite (S-C, 79.1% sulfur, see ESI, Fig.S3†) was prepared according to the method described previously[19]. Sulfur cathode consisted of 80 wt% S-C composite, 10 wt% carbon black (Super P, Timcal) and 10 wt% poly(vinylidene fluoride) (PVDF, 6020 Solef). The sulfur loading on each cathode was ~1.2 mg $cm^{-1}$. Coin cells were assembled in the glove box by using above sulfur cathode, Li foil as anode and Advantec GA55 as separator. The electrolyte amount in each cell was controlled to be ~18 mL $g^{-1}$ (the ratio of electrolyte volume to sulfur content in the cathode).

Firstly, the cyclic voltammetry (CV) for the cell with $Li(G4)_1TFSI$ and $Li(G4)_1TFSI$-4TF are presented in Fig.2a and Fig.2b, respectively. The sweep rate is 0.1 mV $s^{-1}$. All of the cells show two reduction peaks and two very close oxidation peaks (similar to those cases using G4 in electrolyte[20]). The reduction peaks in cathodic scan stand for the reduction of elemental sulfur to soluble PS and then to the insoluble $Li_2S_2/Li_2S$, respectively. And the oxidation peaks in anodic scan represent the formation of PS and the final oxidized active sulfur ($Li_2S_8$ or S), respectively.[20-22] The CV patterns in the first fourth cycles almost overlap each other, indicating steady cycle ability of the cells with the two electrolytes. It should be noted that the second reduction peak is located at higher value and the voltage gap between oxidation and reduction peaks is smaller for the cell with $Li(G4)_1TFSI$-4TF compared to that for $Li(G4)_1TFSI$. TFTFE enhances ion conduction of the electrolyte, thus decreases the over-potential and improves reversibility of the cell.

Fig.2c is the initial potential profiles of the Li-S cells with various electrolytes at 0.1 C between 1.5 V and 3 V. Two plateaus can be clearly observed from the discharge curves, corresponding to two-step reaction of sulfur with metallic Li. The low-potential plateau for $Li(G4)_1TFSI$-xTF reaches ~2.1 V, higher than that for $Li(G4)_1TFSI$ (~2.0 V). Meanwhile, the gaps between discharge plateau and charge plateau of the cells containing TFTFE is smaller than that using pure SIL. These phenomena are well consistent with above CV results. In addition, initial discharge capacity of the cell increases when the amount of TFTFE in the electrolyte increases. Since adding the fluorinated ether can further limit the dissolution of PS at the discharge stage, more active sulfur can be recovered



 

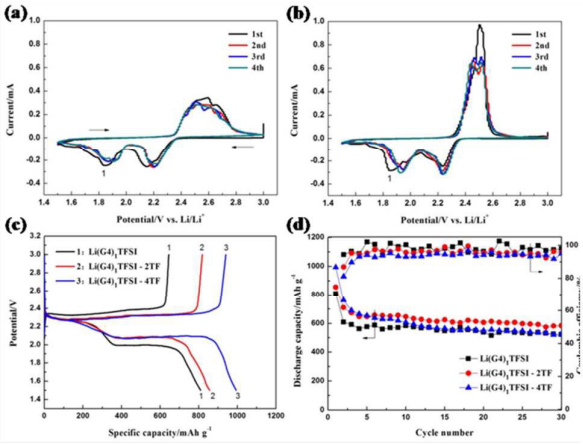


Fig.2 Cyclic voltammogram of the Li-S cell with (a) $Li(G4)_1TFSI$ and (b) $Li(G4)_1TFSI$-4TF at a sweep rate of 0.1 mV $s^{-1}$; (c) initial potential profiles and (d) cycle performances of the cells with various electrolytes at 0.1 C

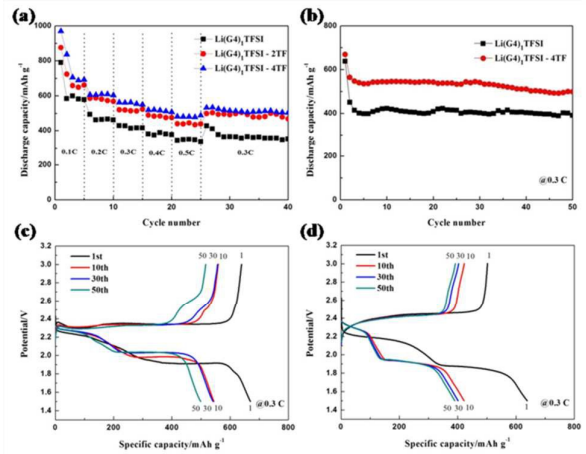


Fig.3 (a) Rate performances of the cells with various electrolytes from 0.1 C to 0.5 C; (b) cycle performances of the cells with various electrolytes at 0.3 C; charge-discharge curves of the cell with (c) $Li(G4)_1TFSI$-4TF and (d) $Li(G4)_1TFSI$ at 0.3 C

reversibly during the subsequent charging process.[23] So TFTFE is beneficial to the utilization of active material.

The cycle performances of Li-S cells with various electrolytes are shown in Fig.2d (more information seen Fig.S4 in ESI†). For the electrolyte containing fluorinated ether, the cell capacity keeps quite stable and the coulombic efficiency approaches 100% after the first cycle, similar to the variation characteristic of the cell with SIL. Obviously, TFTFE existing in SIL indeed won't affect inhibition ability of the electrolyte to PS dissolution and shuttle. The relatively low TFTFE content contributes to more reversible capacity during the whole cycle period, for instance: a reserved capacity of ~580 mAh $g^{-1}$ is obtained after 30 cycles for $Li(G4)_1TFSI$-2TF. But it needs to be recognized that the improvement of TFTFE to the cell performance is a bit insufficient at the current condition. When continuing to increase TFTFE ratio in the SIL, the cycle capability of the cell declines instead, even though the first discharge capacity increases and the coulombic efficiency still keeps in high level. The previous LSV measurement show that the deviation trend enlarges slightly with an increase in TFTFE ratio. So adding more TFTFE may expand negative effect to SIL structure, which in turn weaken the electrochemical stability of the cell.

The electrochemical performances of the cell at high rate are further investigated. The specific capacities at different discharge rates for various electrolytes are presented in Fig.3a (the charge rate is uniformly 0.1 C). The cell capacities using TFTFE-contained electrolytes are always superior to that using pure SIL at each rate. Among them, the cell with $Li(G4)_1TFSI$-4TF exhibits the best rate capability: stable specific capacities of 480 mAh $g^{-1}$ and 500 mAh $g^{-1}$ can be delivered when the current is elevated to 0.5 C and turned back to 0.3 C after 0.5 C cycles, respectively. Since adding TFTFE increases ion conductivity of the electrolyte, the polarization will decline when cell is operated at high-rate conditions. Hence it should be no surprise that the rate performance of the cell is improved remarkably if using TFTFE as support solvent.

The cycle capabilities of the cells with various electrolytes at charge/discharge rate of 0.3 C are compared in Fig.3b. The excellent cycle stability appears in the cell with $Li(G4)_1TFSI$-4TF. The capacity retention after 50 cycles is up to 88.3% based on the second discharge. Moreover, $Li(G4)_1TFSI$-4TF allow the cell to release more capacities than $Li(G4)_1TFSI$ during cycling. The difference of cell performance between two kinds of electrolytes at high rate is more noticeable than that at low rate. Besides, the discharge plateau for $Li(G4)_1TFSI$-4TF also overtops $Li(G4)_1TFSI$ at initial cycle (see ESI, Fig.S5†), demonstrating less over-potentials in the former. The plateau potential ascends step by step and then maintains stable during subsequent cycles in the case of $Li(G4)_1TFSI$-4TF (Fig.3c), which reveals the achievement of a stable electrochemical environment needs a procedure, like other electrolytes using abundant fluorinated ether.[20] While the discharge plateau for $Li(G4)_1TFSI$ is stable all the time (Fig.3d). Therefore, the polarization gap between two electrolytes is further enlarged at latter cycles.

To better understand the function of TFTFE in the cell system, the electrochemical impedance spectroscopy (EIS) of the Li-S cells with various electrolytes was examined. The frequency range of the measurement was $10^5$~0.1 Hz, with the perturbation amplitude of 5 mV. The impedance plots before cycle are composed of a semicircle in medium-to-high frequency and an inclined line in the low frequency (Fig.4a). The former is attributed to the interface charge-transfer resistance ($R_{ct}$), and the latter corresponds to Warburg impedance ($W_o$, associated with $Li^+$ diffusion in the active material). The high-frequency intercept on the real axis represents the ohmic resistance ($R_o$), including the electrolyte and electrode resistances.[24] After 50 cycles, the impedance responses are divided into two obvious semicircles (Fig.4b). The additional semicircle in the high frequency is related to solid-electrolyte interface (SEI) film formed during the charge–discharge process ($R_s$).[25,26] The fitted resistance data according to the corresponding equivalent circuit are shown in Table 1.

The $R_o$ for the cell with fluorinated ether is obviously smaller than the one without it, which is another convincing evidence of TFTFE on promoting ion transport of the electrolyte. The decline in $R_{ct}$ for $Li(G4)_1TFSI$-4TF compared to $Li(G4)_1TFSI$ suggests that the

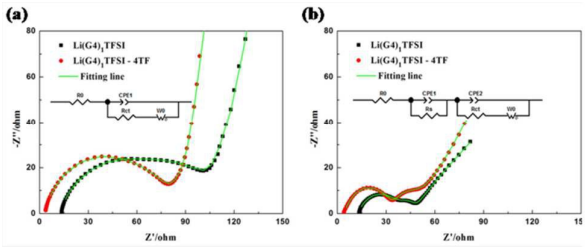


Fig.4 EIS plots of Li-S cells with various electrolytes (a) before cycle and (b) after cycles

Table 1 Fitted resistances data from the equivalent circuit

| Electrolyte | Stage | $R_0$ (Ω) | $R_s$ (Ω) | $R_{ct}$ (Ω) |
|---|---|---|---|---|
| $Li(G4)_1TFSI$ | before cycle | 11.36 | / | 80.64 |
| | after cycles | 12.84 | 25.23 | 8.78 |
| $Li(G4)_1TFSI$-4TF | before cycle | 2.57 | / | 70.71 |
| | after cycles | 4.25 | 30.66 | 6.41 |

electrolyte containing TFTFE is capable of wetting the electrode sufficiently and improving the electrochemical reaction within the cell.[14,25] The increase in $R_s$ is probably associated with film building of TFTFE on Li anode, which can block the access of PS to metallic Li and side-reactions between them.[13] However, whether modified surface film or further reduced PS dissolution should be minor contributing factor for improving cell performance in the high concentration electrolytes, considering that the dissolution and shuttle of PS have already been negligible at this moment. Combining the resistance data with previous electrochemical tests, it can be concluded that the more important role of TFTFE played in the cell system using SIL should be an ionic conduction-enhancing ingredient, especially for high-rate cycle environment.

In summary, we have investigated the effects of adding fluorinated ether on the basic properties of SIL electrolyte and electrochemical performance of Li-S cells. TFTFE meets the demands for support solvent of SIL, including favourable mobility, low dissolution ability of PS and weak interaction with solvate structure, thus is suitable for cooperating with SIL. The cell using the fluorinated ether owns higher reversible capacity than the one without it, accompanied by coulombic efficiency near 100% and quite stable cycle capability. Especially, the low polarization and excellent performance are exhibited in the high-rate measurement of the cell with TFTFE. The capacity retention after 50 cycles is up to 88.3% based on the second discharge at 0.3 C charge-discharge test for $Li(G4)_1TFSI$-4TF. Here, the enhanced ion conduction by TFTFE is mainly contributive for the improvement of the cell performance.

## Acknowledgements

The authors thank the financial support of the National Natural Science Foundation of China (No.21204072). We also thank the support of viscosity measurement provided by the Analytical & Testing Center, Material & Industrial Technology Research Institute, Beijing.

## Notes and references

1 L. Li, Z. Wu, S. Yuan and X.-B. Zhang, Energy Environ. Sci., 2014, 7, 2101-2122.
2 M. K. Song, E. J. Cairns and Y. Zhang, Nanoscale, 2013, 5, 2186-2204.
3 M. Barghamadi, A. S. Best, A. I. Bhatt, A. F. Hollenkamp, M. Musameh, R. J. Rees and T. Rüther, Energy Environ. Sci., 2014, 7, 3902-3920.
4 Y. V. Mikhaylik and J. R. Akridge, J. Electrochem. Soc., 2004, 151, A1969-A1976.
5 S. S. Zhang, J. Power Sources, 2013, 231, 153-162.
6 S. Yoon, Y.-H. Lee, K.-H. Shin, S. B. Cho and W. J. Chung, Electrochim. Acta, 2014, 145, 170-176.
7 X.-B. Cheng, J.-Q. Huang, H.-J. Peng, J.-Q. Nie, X.-Y. Liu, Q. Zhang and F. Wei, J. Power Sources, 2014, 253, 263-268.
8 F. Wu, J. Qian, R. Chen, J. Lu, L. Li, H. Wu, J. Chen, T. Zhao, Y. Ye and K. Amine, ACS Appl. Mater. Interfaces, 2014, 6, 15542-15549.
9 T. Mandai, K. Yoshida, K. Ueno, K. Dokko and M. Watanabe, Phys. Chem. Chem. Phys., 2014, 16, 8761-8772.
10 K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko and M. Watanabe, J. Phys. Chem. B, 2012, 116, 11323-11331.
11 K. Dokko, N. Tachikawa, K. Yamauchi, M. Tsuchiya, A. Yamazaki, E. Takashima, J. W. Park, K. Ueno, S. Seki, N. Serizawa and M. Watanabe, J. Electrochem. Soc., 2013, 160, A1304-A1310.
12 C. Zhang, A. Yamazaki, J. Murai, J.-W. Park, T. Mandai, K. Ueno, K. Dokko and M. Watanabe, J. Phys. Chem. C, 2014, 118, 17362-17373.
13 H. Lu, Y. Yuan, K. Zhang, F. Qin, Y. Lai and Y. Liu, J. Electrochem. Soc., 2015, 162, A1460-A1465.
14 M. Cuisinier, P. E. Cabelguen, B. D. Adams, A. Garsuch, M. Balasubramanian and L. F. Nazar, Energy Environ. Sci., 2014, 7, 2697-2705.
15 L. Suo, Y. Hu, H. Li, M. Armand and L. Chen, Nat. Commun., 2013, 4, 1481.
16 N. Azimi, Z. Xue, I. Bloom, M. L. Gordin, D. Wang, T. Daniel, C. Takoudis and Z. Zhang, ACS Appl. Mater. Interfaces, 2015, 7, 9169-9177.
17 C. Zhang, K. Ueno, A. Yamazaki, K. Yoshida, H. Moon, T. Mandai, Y. Umebayashi, K. Dokko and M. Watanabe, J. Phys. Chem. B, 2014, 118, 5144-5153.
18 K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko and M. Watanabe, J. Am. Chem. Soc., 2011, 133, 13121-13129.
19 J. Li, F. Qin, L. Zhang, K. Zhang, Q. Li, Y. Lai, Z. Zhang and J. Fang, J. Mater. Chem. A, 2014, 2, 13916-13922.
20 H. Lu, K. Zhang, Y. Yuan, F. Qin, Z. Zhang, Y. Lai and Y. Liu, Electrochim. Acta, 2015, 161, 55-62.
21 Y.-S. Su and A. Manthiram, Electrochim. Acta, 2012, 77, 272-278.
22 Z. Dong, J. Zhang, X. Zhao, J. Tu, Q. Su and G. Du, RSC Adv., 2013, 3, 24914-24917.
23 Y. Diao, K. Xie, X. Hong and S. Xiong, Acta Chim. Sinica, 2013, 71, 508-518.
24 F. Qin, K. Zhang, J. Fang, Y. Lai, Q. Li, Z. Zhang and J. Li, New J. Chem., 2014, 38, 4549-4554.
25 Q. Li, Z. Zhang, K. Zhang, J. Fang, Y. Lai and J. Li, J. Power Sources, 2014, 256, 137-144.
26 X. Cui, Z. Shan, L. Cui and J. Tian, Electrochim. Acta, 2013, 105, 23-30.



 