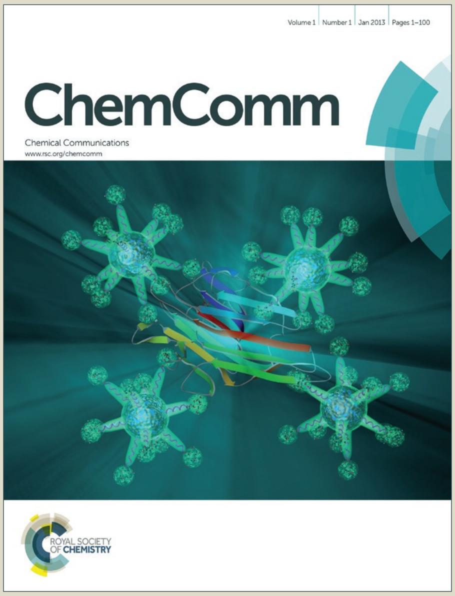
ChemComm

Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications

www.rsc.org/chemcomm

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

A high performance hybrid battery based on aluminum anode and $LiFePO_4$ cathode

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xiao-Guang Sun,[a*] Zhonghe Bi,[a] Hansan Liu,[a] Youxing Fang,[a] Craig A. Bridges,[a] M. Parans Paranthaman,[a] Sheng Dai,[ab] Gilbert M. Brown[a]

A novel hybrid battery utilizing an aluminum anode, a $LiFePO_4$ cathode and an acidic ionic liquid electrolyte based on 1-ethyl-3-methylimidazolium chloride (EMImCl) and aluminum trichloride ($AlCl_3$) (EMImCl-$AlCl_3$, 1-1.1 in molar ratio) with or without $LiAlCl_4$ is proposed. The hybrid ion battery delivers an initial high capacity of 160 mAh g^{-1} at a current rate of C/5. It also shows good rate capability and cycling performance.

The environmental concerns over the use of fossil fuels and their limited resources, combined with energy security concerns, have spurred great interest in energy harvesting from renewable sources such as wind and solar.[1] However, both solar and wind are intermittent, and hence, in order to effectively utilize these renewable energies, low-cost electric energy storage (EES) devices are needed. Among various EES technologies, lithium ion batteries have been dominant in the electronic markets such as cellular phones, laptop computers and electric vehicles, and therefore, they are also good candidates for and grid and stationary applications. However, one major issue is the high cost. As an alternative, cheap and naturally abundant elements based technologies such as sodium ion, magnesium ion and aluminum ion batteries have been intensively studied during the last few years.[2] Among these emerging technologies, aluminum batteries have distinct advantages because its three electron redox couple provides a high theoretical specific capacity of 2980 mAh g^{-1} and a high volumetric capacity of 8040 mAh cm^{-3}.

However, the development of rechargeable aluminum ion batteries faces major challenges from both electrolyte and cathode. Because of the low reduction potential of aluminum (-1.68 V vs. standard hydrogen electrode), aqueous electrolytes cannot be used as hydrogen will be generated before aluminum can be plated during the reduction process. So far, it has been shown that aluminum deposition/stripping is only possible in acidic ionic liquids based on mixtures of anhydrous $AlCl_3$ with organic halide salts such as EMImCl and N-(1-butyl)pyridinium chloride etc.[3] However, the strong acidic nature of the ionic liquids poses stringent requirement for the hardwares of the aluminum batteries, as it was shown that corrosion was readily occurred to stainless steels.[4] Fortunately, there are some recent reports on the development of new electrolytes exhibiting reversible aluminum deposition/stripping by replacing organic chloride salts with bis(trifluoromethanesulfonyl)imide (TFSI) based ionic liquids, neutral ligand based complexes, and organic solvents.[5] These alternative electrolytes hopefully can alleviate the corrosion problem to some extents. On the other hand, the challenge facing the aluminum cathodes results from its own advantage, i.e. trivalent cation, which makes its intercalation/de-intercalation very difficult.[6] Other challenges facing aluminum ion batteries are low cell voltage and poor cycling performance.[7] Recently, two groups led by Dai and Jiao et al reported good cycling performance on high voltage rechargeable aluminum ion batteries utilizing three-dimensional graphitic-foam and carbon paper as the cathode, respectively.[2i, 8] Besides aluminum ion batteries, Chang et al. reported good cycling performance on an asymmetric

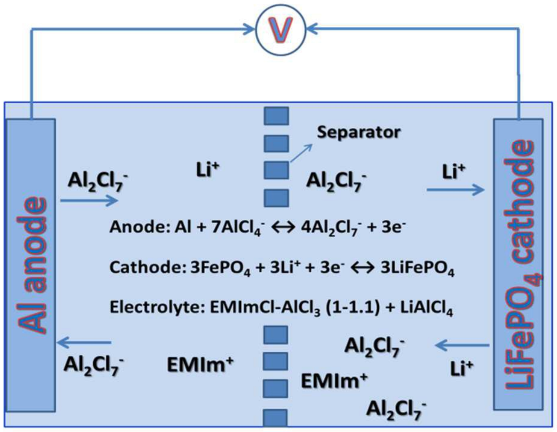


Fig. 1. Schematic illustration of the hybrid battery with Al as the anode, $LiFePO_4$ as the cathode and acidic ionic liquid as the electrolyte.

---

[a] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. E-mail: sunx@ornl.gov; Fax: +1 865 576 5152; Tel: +1 865 241-8822.
[b] Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of experiment and addition cycling data]. See DOI: 10.1039/x0xx00000x

ChemComm Accepted Manuscript

capacitor based on Prussian blue and active carbon electrodes in an aqueous electrolyte.[9] However, the reported capacities for the aforementioned batteries and capacitors were low, i.e. below 100 mAh g^{-1}. Herein we report a new rechargeable battery based on the hybrid chemistries of aluminum anode and lithium intercalation cathode $LiFePO_4$, which exhibits high capacity, good rate capability and cycling performance.

Fig. 1 illustrates the principle of such a hybrid battery in an acidic ionic liquid electrolyte based on EMImCl and $AlCl_3$ (1-1.1 in molar ratio). Fig. 2a shows that the slightly acidic electrolyte still supports reversible aluminium deposition/stripping, which is the foundation for the operation of this hybrid battery. For this hybrid battery, the electrochemical redox reactions are reversible aluminum deposition/stripping at the anode and lithium intercalation/de-intercalation at the cathode during charge-discharge process. The overall cell reactions can be described as following:

Anode: $Al + 7LiAlCl_4 - 3e^- \leftrightarrow 4LiAl_2Cl_7 + 3Li^+$

Cathode: $3FePO_4 + 3Li^+ + 3e^- \leftrightarrow 3LiFePO_4$

Overall: $Al + 7LiAlCl_4 + 3FePO_4 \leftrightarrow 4LiAl_2Cl_7 + 3LiFePO_4$

Similar concept has been proposed by us several years ago using λ–MnO_2 as the cathode.[10] However, low capacity and poor cycling performance were observed, probably due to the acidic nature of the electrolyte caused corrosive side reactions with possible gradual dissolution of the cathode material. Since then, we have made several modifications to improve the cycling performance of this new hybrid battery. Firstly, to avoid corrosion of the current collector, E-Tek carbon cloth was used as the substrate on which the cathode slurry composed of 70 wt% $LiFePO_4$, 15 % Super P carbon (C45) and 15 wt% poly(tetrafluoroethylene) (PTFE) was evenly coated. Fig. S1 confirms that the carbon cloth does not contribute to the overall cell capacity. Secondly, an insulating shallow cup made of polyethylene was used as an internal container for the cathode electrode and the acidic electrolyte soaked in a carbon fibre paper. The cup was designed to fit inside the coin cell sealing gasket. Thirdly, a thin platinum wire was used as a bridge between the cathode and the coin cell base. To avoid shorting the coin cell during cramping, the wire was wrapped with Celgard at the edge of the cup. Finally, a fixed amount of 80 μl electrolyte was used for assembling the coin cells. This amount of electrolyte was enough to wet the cathode and the separator but avoided flooding the shallow cup.

In principle, lithium salt is not needed in this new hybrid battery,[10] since the lithium ion extracted from the $LiFePO_4$ cathode during the charge process will sustain the necessary electrochemical reaction in the following cycles. To confirm this, a cyclic voltammetry was performed on an Al||$LiFePO_4$ coin cell using the pure acidic ionic liquid, EMImCl-$AlCl_3$ (1-1.1). Fig. 2b shows that indeed reversible redox peaks are observed, except that the first lithium de-intercalation peak at 1.97 V is well separated from the rest of the peaks. In the second cycle the lithium de-intercalation peak decreases to 1.80 V whereas the lithium intercalation occurs at 1.18 V. The coulombic efficiencies for the first two cycles are 66.7% and 82.35%, respectively. After ten cycles, the lithium de-intercalation and intercalation process are stabilized at 1.6 and 1.2 V, respectively, with a coulombic efficiency of 82.33%. To check whether the large peak separation and low coulombic efficiencies are due to the lack of lithium salt in the electrolyte, 1.0 M $LiAlCl_4$ was added to the acidic ionic liquid electrolyte and CV was carried out under the same condition. Fig. 2a shows that the acidic electrolyte with 1.0 M $LiAlCl_4$ still supports reversible aluminium deposition/stripping except that slightly lower current density than that without the lithium salt is observed, probably due to the increased viscosity of the solution. It should be pointed out that it is impossible to form Al-Li alloy in the acidic ionic liquid

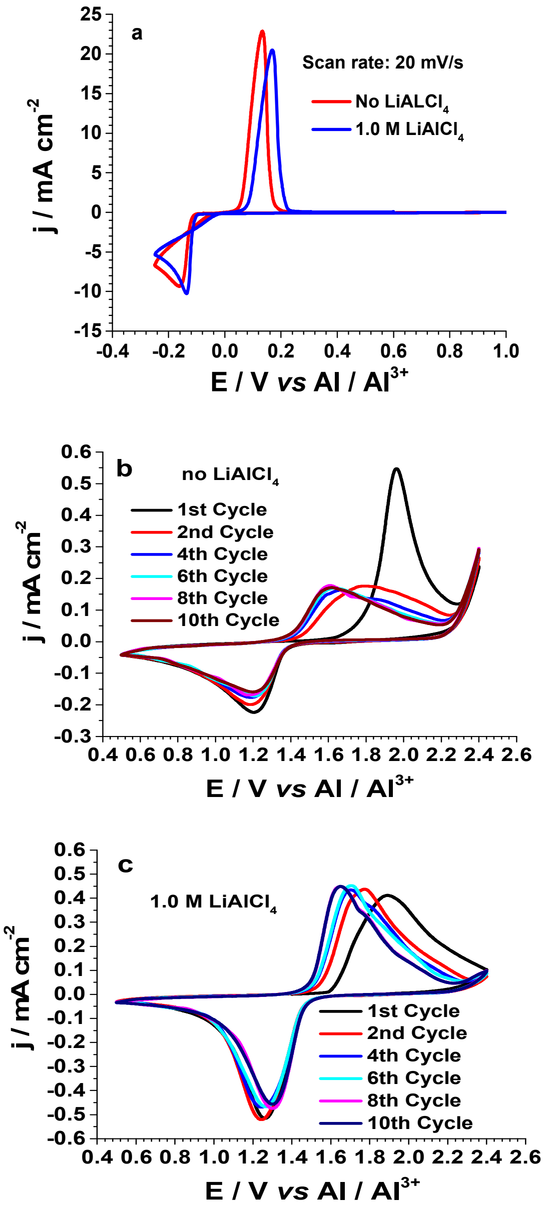


Fig. 2. a) Cyclic voltammetry of Pt working electrode in EMImCl-$AlCl_3$ (1-1.1) with and without 1.0 M $LiAlCl_4$ at a scan rate of 20 mV/s (aluminum coil and aluminum wire were used as counter and reference electrode, respectively). Cyclic voltammetry of Al||$LiFePO_4$ coin cell in b) EMImCl-$AlCl_3$ (1-1.1) and c) EMImCl-$AlCl_3$ with 1.0M $LiAlCl_4$ at a scan rate of 0.1 mV/s.

ChemComm Accepted Manuscript

electrolyte containing $LiAlCl_4$, since the potential for aluminium deposition is well above that for the alloy formation and the instability of lithium in the acidic media (Fig. S2).[11] As shown in Fig. 2c, with the presence of $LiAlCl_4$ the lithium de-intercalation process decreases to 1.89 V whereas the intercalation process increases to 1.28 V. In addition, the initial coulombic efficiency reaches a high value of 90.4%. After ten cycles, the corresponding lithium de-intercalation and intercalation process are stabilized at 1.64 and 1.3 V, respectively, maintaining a high coulombic efficiency of 96.0%. The decreased lithium de-intercalation potential coupled with the increased intercalation potential for the one with $LiALCl_4$ indicates that the presence of lithium salts improves the kinetics of the lithium reaction in the electrode. It is also noted in Fig. 2b and c that the current density with lithium salt almost doubles that without the lithium salt, which can translate into higher capacity for the former under the same current rate as shown later. Similar effect has been observed for a hybrid Mo_6S_8/Mg battery with all-phenyl complex (APC) and LiCl dissolved in THF as the electrolyte.[12] It is further noticed in Fig. 2b and c that there is an onset oxidation around 2.25 V. Thus, to avoid these side reactions, the cell voltage was cut off at 2.2 V during the charge process.

To further confirm whether the lithium intercalation is the major cathode reaction during the discharge process, $Li||LiFePO_4$ half-cells were assembled using Swagelok cells with 1.0 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethylene carbonate (DEC) (1/1/1 in volume) as the electrolyte. The cells were charged under a current of 50 μA until the cell voltage reached 4.0 V, after which they were held constant until the current was decreased to less than 5 μA. After delithiation, the electrodes were disassembled and washed inside the glovebox with DMC for three times before drying under vacuum. The dried $FePO_4$ electrodes were then used to assemble $Al||FePO_4$ cells, which were discharged under a constant current of 50 μA. As shown in Fig S3a and b, the cell without $LiAlCl_4$ takes less than 0.6 hr whereas the one with $LiAlCl_4$ takes 3.8 hrs to reach 0.5 V. The well levelled cell voltage at 1.35 V for the latter reminds the typical discharge profile of $FePO_4$ electrode. The dramatic difference in discharge performance in Fig. S3 confirms that indeed Li^+ ion intercalation/de-intercalation is the main cathode reaction in the hybrid battery. However, it should be mentioned that the voltage observed for the hybrid battery is well below the theoretical value, that is, 3.5 – (3.05 - 1.68) = 2.13 V. Similarly, for the hybrid battery based on high voltage MnO_2, a voltage of 2.15 V was observed, which was also far below the theoretical value of 4.0 - (3.05 - 1.68) = 2.63 V.[10] The exact reasons for the observed low cell voltages are not known now, which might be closely related to the specific electrolyte system and deems investigation in the further studies.

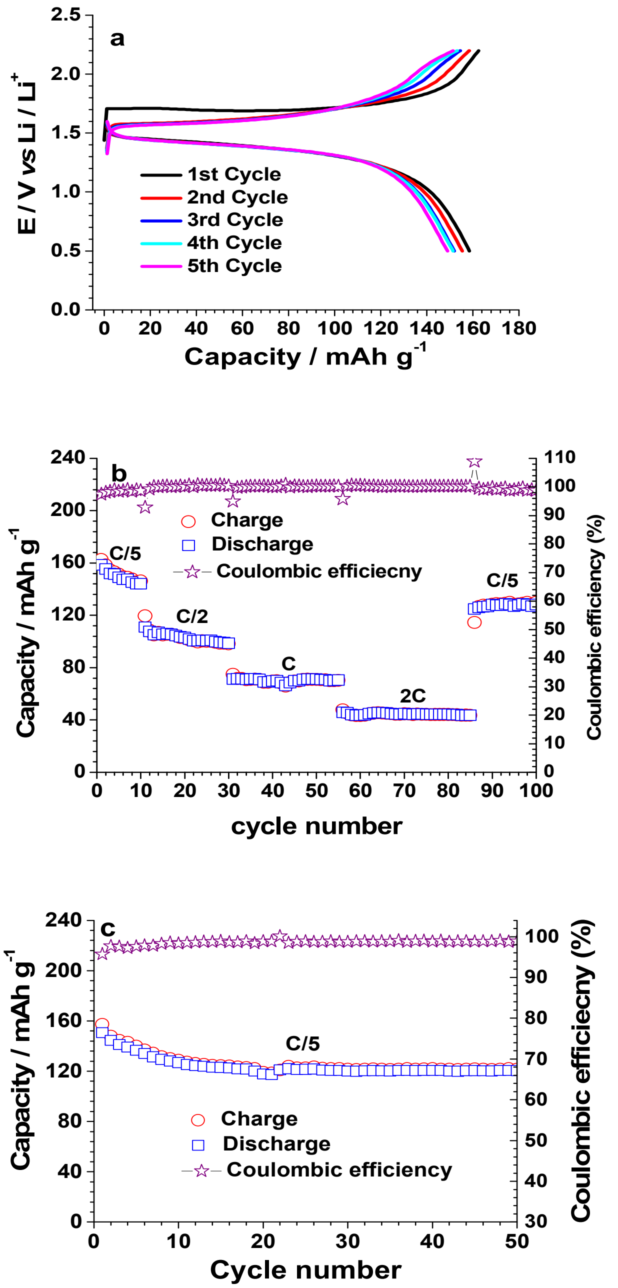


Fig. 3. a) Charge-discharge profile of a hybrid battery in the EMImCl-$AlCl_3$ (1-1.1) electrolyte containing 1 M $LiALCl_4$ under a current rate of C/5; b) charge and discharge capacities and coulombic efficiencies of the hybrid battery at different current rates; c) charge and discharge capacities and coulombic efficiencies of a hybrid battery using the same electrolyte at a current rate of C/5.

Fig. 3a shows the typical charge-discharge profile of the first five cycles of a hybrid battery using the acidic ionic liquid electrolyte containing 1.0 M $LiAlCl_4$ at a current rate of C/5. The charge and discharge capacities are 162.6 and 158.5 mAh g^{-1} respectively, resulting in a high coulombic efficiency of 97.5%. The flat charge/discharge profiles in the first cycle are typical behaviour of $LiFePO_4$ in traditional carbonate electrolytes, except that there is a 0.2 V difference between the charge and discharge process, as has been noticed in the CVs (Fig.2). The overpotential in the charge process decreases after the first cycle, indicating an initial activation process within the electrode. Fig. 3b shows the rate capability of the hybrid battery. Under a current rate of C/5, the reversible capacity gradually decreases to 144.1 after 10 cycles. When the current rate is increased to C/2, the charge and discharge capacities are decreased to 119.6 and 111.0 mAh g^{-1}, respectively, which are gradually decreased to 99 mAh g^{-1} after 20 cycles. With the current rate being further increased to C

ChemComm Accepted Manuscript

and 2C, the reversible capacities are decreased to 71 and 44 mAh g^{-1}, respectively. However, once the current rate is decreased to C/5, the reversible capacity is recovered to a high value of 127 mAh g^{-1}. Fig. 3c shows the cycling stability of another fresh hybrid battery cycled under a current rate of C/5. Similar to that observed in Fig. 3b, the reversible capacities gradually decrease in the first few cycles, after which they are stabilized and are still as high as 122 mAh g^{-1} after 50 cycles. As a comparison, the hybrid batteries using pure acidic EMImCl-$AlCl_3$ electrolyte deliver lower capacities under similar current rates (Fig. S4). This result is consistent with the CV data presented in Fig. 2 and is also similar to the result of a hybrid Mo_6S_8/Mg battery without addition of LiCl. [12] However, it should be mentioend that the low coulombic efficiencies observed in the CV (Fig. 2b) and the cycling data (Fig. S4) for the hybrid cells using pure acidic ionic liquids are mainly due to the trapping of lithium in the electrolyte after charge, which is not available for intercalation during the discharge process. Similarly, the initial capacity decreases observed for the cells with and without $LiAlCl_4$ (Figs. 3 and S4) are also due to the trapping of lithium, but the decrease in the latter is accelerated due to the lack of lithium salt in the electrolyte.

In summary, we have demonstrated that coupling aluminum and lithium chemistry in one device can deliver high capacity and good cycling performance. The safe nature and earth abundance of aluminum, coupled with the safety of ionic liquid electrolytes [13] make this new kind of hybrid battery very attractive for grid and stationary applications. The recent development of new ionic liquids electrolytes exhibiting reversible aluminum deposition/stripping offers new opportunity for rechargeable aluminum ion batteries, which yet needs to be confirmed in the future. [5c, 5d, 5f-i]

This research was supported by the U.S. Department of Energy's Office of Science, Basic Energy Science, Materials Sciences and Engineering Division.

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 (a) Z. G. Yang, J. L. Zhang, M. C. W. Kintner-Meyer, X. C. Lu, D. W. Choi, J. P. Lemmon and J. Liu, *Chemical Reviews*, 2011, **111**, 3577; (b) J. B. Goodenough, H. D. Abruna and M. V. Buchanan, in *Basic Research Needs for Electrical Energy Storage*, 2007.

2 (a) B. L. Ellis and L. F. Nazar, *Current Opinion in Solid State & Materials Science*, 2012, **16**, 168; (b) H. Pan, Y.-S. Hu and L. Chen, *Energy & Environmental Science*, 2013, **6**, 2338; (c) S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder and K. Kang, *Advanced Energy Materials*, 2012, **2**, 710; (d) N. Yabuuchi, K. Kubota, M. Dahbi and S. Komaba, *Chemical Reviews*, 2014, **114**, 11636; (e) P. Saha, M. K. Datta, O. I. Velikokhatnyi, A. Manivannan, D. Alman and P. N. Kumta, *Progress in Materials Science*, 2014, **66**, 1; (f) R. Mohtadi and F. Mizuno, *Beilstein Journal of Nanotechnology*, 2014, **5**, 1291; (g) J. Muldoon, C. B. Bucur and T. Gregory, *Chemical Reviews*, 2014, **114**, 11683; (h) H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour and D. Aurbach, *Energy & Environmental Science*, 2013, **6**, 2265; (i) M. C. Lin, M. Gong, B. Lu, Y. Wu, D. Y. Wang, M. Guan, M. Angell1, C. Chen, J. Yang, B. J. Hwang and H. Dai, *Nature*, 2015, **520**, 324; (j) Q. Li and N. J. Bjerrum, *J. Power Sources*, 2002,, **110**, 1; (k) S. Yagi, T. Ichitsubo, Y. Shirai, S. Yanai, T. Soi, K. Murase and E. Matsubara, *J. Mater. Chem. A*, 2014, **2**, 1144.

3 (a) Q. Liao, W. R. Pitner, G. Stewart, C. L. Hussey and G. R. Stafford, *J. Electrochem. Soc.*, 1997, **144**, 936; (b) Y. G. Zhao and T. J. VanderNoot, *Electrochimica Acta*, 1997, **42**, 3.

4 L. D. Reed and E. Menke, *J. Electrochem. Soc.*, 2013, **160**, A915−A917.

5 (a) H. M. Abood, A. P. Abbott, A. D. Ballantyne and K. S. Ryder, *Chem. Commun. (Camb)*, 2011, **47**, 3523; (b) F. Endres, *Chemphyschem*, 2002, **3**, 144; (c) S. Z. El Abedin and F. Endres, *Chemphyschem*, 2006, **7**, 58; (d) A. P. Abbott, R. C. Harris, Y.-T. Hsieh, K. S. Rydera and I. W. Sun, *Physical Chemistry Chemical Physics*, 2014, **16**, 14675; (e) F. Coleman, G. Srinivasan and M. Swadzba-Kwasny, *Angewandte Chemie-International Edition*, 2013, **52**, 12582; (f) Y. X. Fang, X. G. Jiang, X. G. Sun and S. Dai, *Chem. Comm.*, 2015, **51**, 13286 ; (g) Y. X. Fang, K. Yoshii, X. G. Jiang, X. G. Sun, T. Tsuda, N. Mehio and S. Dai, *Electrochimica Acta*, 2015, **160**, 82; (h) Y. Nakayama, Y. Senda, H. Kawasaki, N. Koshitani, S. Hosoi, Y. Kudo, H. Morioka and M. Nagamine, *Physical Chemistry Chemical Physics*, 2015, **17**, 5758; (i) X. G. Sun, Y. X. Fang, X. G. Jiang, K. Yoshii, T. Tsuda and S. Dai, *Chem. Comm.*, 2015, DOI: 10.1039/C5CC06643C

6 M. P. Paranthaman, H. Liu, X. G. Sun, S. Dai and G. M. Brown, in *Advances in batteries for medium and large-scale energy storage*, ed. A. Davies, Woodhead Publishing Ltd., 2015.

7 (a) N. Jayaprakash, S. K. Das and L. A. Archer, *Chem. Commun.*, 2011, **47**, 12610−12612; (b) J. V. Rani, V. Kanakaiah, T. Dadmal, M. S. Rao and S. Bhavanarushi, *J. Electrochem. Soc.*, 2013, **160**, A1781−A1784; (c) N. S. Hudak, *J. Phys. Chem. C,* , 2014, **118**, 5203; (d) H. L. Wang, Y. Bai, S. Chen, X. Y. Luo, C. Wu, F. Wu, J. Lu and K. Amine, *Acs Applied Materials & Interfaces*, 2015, **7**, 80; (e) L. X. Geng, G. C. Lv, X. B. Xing and J. C. Guo, *Chem. Mater.*, 2015, **27**, 4926.

8 H. B. Sun, W. Wang, Z. J. Yu, Y. Yuan, S. Wang and S. Q. Jiao, *Chemical Communications*, 2015, **51**, 11892.

9 Z. Li, K. Xiang, W. T. Xing, W. C. Carter and Y. M. Chiang, *Advanced Energy Materials*, 2015, **5**.

10 G. M. Brown, M. P. Paranthaman, S. Dai, N. J. Dudney, A. Manthiram, T. J. McIntyre and X. G. Sun, *US patent*, 2012, **US 2012/0082904A1**.

11 Y. S. Fung and H. C. Lai, *J. Appl. Electrochem.*, 1989, **19**, 239.

12 Y. Cheng, Y. Shao, J. Zhang, V. L. Sprenkle, J. Liu and G. Li, *Chem. Commun.*, 2014, **50**, 9644.

13 (a)M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621; (b) X. G. Sun and S. Dai, *Electrochimica Acta*, 2010, **55**, 4618.

ChemComm Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx