

View Article Online View Journal

# **RSC Advances**

This article can be cited before page numbers have been issued, to do this please use: Y. Bi, T. Wang, M. Liu, R. Du, W. Yang, Z. Liu, Z. Peng, Y. Liu, D. Wang and X. Sun, *RSC Adv.*, 2016, DOI: 10.1039/C6RA00648E.



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. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this 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 <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> 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.



www.rsc.org/advances

Published on 02 February 2016. Downloaded by University of Connecticut on 02/02/2016 17:01:07.



### COMMUNICATION

## Stability of Li<sub>2</sub>CO<sub>3</sub> in Cathode of Lithium Ion Battery and Its Influence on Electrochemical Performance

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

Yujing Bi<sup>a,b,d</sup>, Tao Wang<sup>c</sup>, Meng Liu<sup>a</sup>, Rui Du<sup>a,b</sup>, Wenchao Yang<sup>a</sup>, Zixuan Liu<sup>a</sup>, Zhe Peng<sup>a</sup>, Yang Liu<sup>a</sup>, Deyu Wang<sup>a</sup>, \*, Xueliang Sun<sup>d</sup>

www.rsc.org/

\_\_\_\_

Lithium carbonate is one of the unavoidable impurities in cathode side. It could chemically react with LiPF<sub>6</sub> based electrolyte and LiPF<sub>6</sub> powder to produce LiF & CO<sub>2</sub>, although it presents the excellent electrochemical inertness. The samples of Li<sub>2</sub>CO<sub>3</sub>-coated and LiF-coated LiNi<sub>0.8</sub>CO<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> are prepared to compare their influence on cathode's behavior. After 200 cycles at 1C, in contrast to 37.1% of capacity retention for the Li<sub>2</sub>CO<sub>3</sub>-coated material, the LiF-coated LiNi<sub>0.8</sub>CO<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> still retains 91.9% of the initial capacity, which is similar to the fresh sample. It demonstrates that Li<sub>2</sub>CO<sub>3</sub>'s decomposition could seriously deteriorate the cyclic stability if it is taken place during working.

#### Introduction

Lithium ion battery (LIB) was the most successfully electrochemical energy storage technology in the past decades. As a chemical system, its performance should be significantly influenced by the impurities, including the species brought by the components or *insitu* generated during working.<sup>1-5</sup> The good understanding on their chemical behavior and influence on cell performance should be particularly important to develop high-quality commercial batteries.

In cathode side, lithium carbonate is one of the unavoidable impurities due to the carbonate-based electrolyte and the metastability of cathode materials.<sup>6-9</sup> Li<sub>2</sub>CO<sub>3</sub> possessed the good electrochemical inertness, so that it was considered as one of the component to construct the cathode's protective layer.<sup>10-12</sup> In other hand, its appearance was often accompanied with the serious capacity fading of cathode materials, especially for nickel rich layer oxides.<sup>13-16</sup> This contradiction, namely the role of lithium carbonate, was not carefully investigated till date in our best knowledge.

Here we research the stability of lithium carbonate on

This journal is © The Royal Society of Chemistry 20xx

cathode side, and its influence on electrochemical performance of  $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ . Although it possesses the excellent electrochemical inertness, the exposed  $Li_2CO_3$  particles are easily reacted with LiPF<sub>6</sub> based electrolyte and LiPF<sub>6</sub> powder to generate LiF, CO<sub>2</sub> and POF<sub>3</sub>. To compare the influence of this reaction, the samples of  $Li_2CO_3$ -coated and LiF-coated  $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  are prepared. In contrast to the poor cyclic stability of  $Li_2CO_3$ -coated material, LiF-coated sample presents much better cyclic stability, which is similar to the fresh pristine materials.

#### **Experimental section**

LiPF<sub>6</sub> (Kanto Chemical Co., Inc., 99%), LiTFSI (MMM, Ltd., 98%), and Li<sub>2</sub>CO<sub>3</sub> (Aladin, >99%) were dried at 120 °C under vacuum in transfer chamber of Ar-glove box for 48 h before used. The electrolyte of 1 molL<sup>-1</sup> LiPF<sub>6</sub> dissolved in the mixed solution of propyl carbonate (PC) and dimethyl carbonate (DMC) (1:1, v/v) (Guotai Huarong Chemical New Material Co., Ltd.) was directly used as received.

The chemical stability of Li<sub>2</sub>CO<sub>3</sub> was evaluated by immersing the powder material (1 g) into 5 mL electrolyte, sealed into Al-plastic packages, and then heated at 30, 55, 80 and 100  $^{\circ}$ C for 12 h in Arglove box respectively. The powder of Li<sub>2</sub>CO<sub>3</sub> (0.49 g) and LiPF<sub>6</sub> (2 g) were also mixed and sealed into Al-plastic packages to heat at 80  $^{\circ}$ C for 12 h. To check the interactions between water and LiPF<sub>6</sub>, 10 mL H<sub>2</sub>O is slowly dropped onto 2 g LiPF<sub>6</sub> powder. Moreover, 2 g LiPF<sub>6</sub> powder is fast dissolved into 10 mL H<sub>2</sub>O.

 $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  was synthesized by the high-temperature solid-state method as published.<sup>16,17</sup> The  $Li_2CO_3$ -coated  $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  was obtained by storing  $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  at 55 °C with saturated stream (15 kPa) in desiccator for one month. The LiF-coated  $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  was prepared by immersing the  $Li_2CO_3$ -coated sample into the electrolyte and heat at 80 °C for 12 h.

<sup>&</sup>lt;sup>a.</sup> Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China

<sup>&</sup>lt;sup>b.</sup> University of Chinese of Academy of Sciences, Beijing, 100049, China

<sup>&</sup>lt;sup>c</sup> Shanghai Institute of Space Power Source, Shanghai, 200245, China.

<sup>&</sup>lt;sup>d.</sup> Nanomaterial and Energy Lab, Department of Mechanical and Materials

Engineering, University of Western Ontario, London, Ontario, N6A 5B9, Canada

<sup>\*</sup> Corresponding author: wangdy@nimte.ac.cn

The electrode was composed of cathode material, super P and polyvinylidenefluoride (PVdF) at the weight ratio 8:1:1 suspended in NMP and the slurry was casted on aluminum foil current collectors.

Electrode was dried at 120 °C under vacuum for 12 h and then punched into  $\phi$ 16 mm disks. CR2032 coin cells were assembled with the prepared electrode as cathode, lithium foil as anode, Celgard 2550<sup>®</sup> as separator and 1 molL<sup>-1</sup> LiPF<sub>6</sub> in mixture solution of poly carbonate (PC)/dimethyl carbonate (DMC) (1:1, v/v) as electrolyte. The cells assembly was performed in Ar-filled M-Braun glove box, where H<sub>2</sub>O and O<sub>2</sub> were controlled less than 1 ppm. Linear sweep voltammetry between 2.5-5.5 V vs. Li/Li<sup>+</sup> at 0.1 mV/s rate is carried out on electrochemical work station (Solartron, 1470E). The electrochemical measurements were performed on battery tester of Land 2001A (Wuhan, China) between 2.8-4.3 V vs. Li/Li<sup>+</sup> at 25 °C under various rates.

The powders were characterized by X-ray diffraction with Bruker D8 advanced diffractometer using CuK $\alpha$  ( $\lambda$ = 1.5406Å) radiation (Bruker AXS, D8 Advance) between 10-60° by 0.02° step. The analysis of microscopy was performed with scanning electron microscopy (SEM, Hitachi, S4800) and transmission electron microscopy (TEM, FEI, Tecnai F20, 200 kV). Surface analysis was conducted with a PHI 3056 X-ray photoelectron spectrometer (XPS) which was excited by an Mg  $K\alpha$  radiation at a constant power of 100 W (15 kV and 6.67 mA). The gases species were analyzed on gas chromatograph mass spectrometer (GC-MS, Agilent 7890B-5977A, EI). The column of GC is capillary column chromatograph (Agilent, HP-PLOT/U).

#### **Results and Discussion**

Published on 02 February 2016. Downloaded by University of Connecticut on 02/02/2016 17:01:07

The purchased lithium carbonate could be attributed to the C2/c space group of monoclinic system with particles size at  $2\sim10$  µm, as shown in Fig.1a. It presents a good electrochemical inertness, which decomposition reaction is peaked at ~5.3 V vs. Li/Li<sup>+</sup> as shown in Fig.1b. Obviously, Li<sub>2</sub>CO<sub>3</sub> is electrochemically stable inside of lithium ion cells in current working conditions.



**Figure 1** Characterization of commercial Li<sub>2</sub>CO<sub>3</sub> powder (a) XRD pattern and SEM image (b) linear sweep voltammetry with Li<sub>2</sub>CO<sub>3</sub> electrode as working electrode, Li foil as counter and reference electrode, and scanned with 0.1 mVs<sup>-1</sup>



Figure 2 (a) XRD patterns comparison of Li<sub>2</sub>CO<sub>3</sub> immersed in electrolyte at 30 °C for 2 days and 4 weeks; (b) XRD patterns comparison of Li<sub>2</sub>CO<sub>3</sub> heating in electrolyte at 55, 80, 100 °C for 12 h; (c) GC-MS results and digital pictures of Al-plastic package before and after heating (1# , 2#); (d) digital pictures of LiPF<sub>6</sub> crystal dissolved by different ways (1) LiPF<sub>6</sub> powder is fast dissolved in to water, 2) water is slowly dropped onto LiPF<sub>6</sub> crystal)

The chemical stability of Li<sub>2</sub>CO<sub>3</sub> is evaluated via the experiment that the mixture of 1 g Li<sub>2</sub>CO<sub>3</sub> and 5 mL electrolyte was sealed in an Al-plastic package and heated at 30, 55, 80, 100 °C, respectively. When treated at 30 °C, the signal of Li<sub>2</sub>CO<sub>3</sub> is gradually weakened as the time prolonged, as shown in Fig. 2a. In contrast, LiF peaks are detectable after 2 days storage, and their intensities are obviously strengthened after 30 days. As the temperature increasing to 55 °C, lithium fluoride is one of the dominant phases after 12 h heat treatment. As the sample treated at 80 °C and 100 °C after 12 h, LiF becomes the single crystalline phase in Fig. 2b. It indicates that Li<sub>2</sub>CO<sub>3</sub> should chemically react with LiPF<sub>6</sub> to generate lithium fluoride as the solid product.

Published on 02 February 2016. Downloaded by University of Connecticut on 02/02/2016 17:01:07

View Article Online DOI: 10.1039/C6RA00648E COMMUNICATION

#### Journal Name

The generated gas in the package is tested by GC-MS. In all tested packages,  $CO_2$  and  $POF_3$  are the extremely dominant gaseous species, which take a ratio more than 90%, as demonstrated in Fig. 2c. Carbon dioxide should be decomposed from Li<sub>2</sub>CO<sub>3</sub>, and POF<sub>3</sub> could be attributed to the reaction of  $PF_6^-$  group with the trace amount of moisture.<sup>18</sup> Small chromatographic peaks at 9, 13 min and 16.2 min would be caused by the corrosion of HF. Combined with the XRD results, lithium carbonate should be spontaneously reacted with electrolyte to generate LiF as the solid product,  $CO_2$  and  $POF_3$  as the gaseous species.

To further explore the probable reason of this reaction, the mixture of  $Li_2CO_3$  and  $LiPF_6(1:1$  in mole) powder were sealed and heated at 80 °C for 12 h. The tested packages were inflated quickly. The solid remnant is LiF and the dominant gaseous products are POF<sub>3</sub> and CO<sub>2</sub>, indicating this reaction between solids is same as  $Li_2CO_3$  with electrolyte. This result probably indicates that the  $Li_2CO_3$  decomposition could be preceded with the direct attack of  $LiPF_6$  without the assistance of moisture, as shown in Pathway 1, because both salts are extremely dried before the test.

Pathway1:  $LiPF_6 + Li_2CO_3 \rightarrow POF_3 + CO_2 + 3LiF$ 

According to LiPF<sub>6</sub> production procedure, it should contain trace amount of HF,<sup>19</sup> which could react with lithium carbonate to produce water. Although they are capable to react with water in organic media,  $PF_6^-$  groups are quite stable in aqueous solution, e.g.,  $NaPF_6^$ aqueous solution utilized as the source of  $PF_6^-$  in the synthesis of ionic liquids.<sup>20</sup> The stability of LiPF<sub>6</sub> powder with small amount of water, the situation in this case, is not discussed in our best knowledge.

Here dissolution behavior of LiPF<sub>6</sub> salt (2 g) in water (10 mL) is compared with the experiments of quickly pouring LiPF<sub>6</sub> powder into water and slowly dropping water into LiPF<sub>6</sub> powder. In the first case, it forms the clear solution with a pH value of ~5, as shown in Fig. 2d-1. In the second case, smoke is released when water was encountered to LiPF<sub>6</sub> powder. After dropping, the solution still contains some insoluble stuff, as demonstrated in Fig. 2d-2, which is lithium fluoride identified by XRD. The pH value of solution is ~2, indicating H<sup>+</sup> was generated during dissolving. It demonstrates that LiPF<sub>6</sub> tends to decompose with small amount of H<sub>2</sub>O to generate H<sup>+</sup>. The probable reason for this phenomenon should be that PF<sub>6</sub><sup>-</sup> ion group couldn't form the stable hydration layer with small amount of H<sub>2</sub>O.<sup>21-24</sup> Therefore trace amount of HF may catalyze the decomposition of lithium carbonate with H<sup>+</sup> as the catalyst, as shown in Pathway 2. This mechanism is still possible although we tend to believe Patherwayl is more reasonable.

Pathway2:  $2H^+$  + Li<sub>2</sub>CO<sub>3</sub>  $\rightarrow$  2Li<sup>+</sup> + CO<sub>2</sub> +  $H_2O$ 

 $\text{LiPF}_6 + 2\text{Li}^+ + H_2O \rightarrow \text{POF}_3 + 2H^+ + 3\text{LiF}$ 

The chemical stability of Li<sub>2</sub>CO<sub>3</sub> with LiTFSI electrolyte and LiTFSI powder was also evaluated to compare the influence of cations. No obvious inflation was observed after storing at 80 °C for 12 h, indicating Li<sub>2</sub>CO<sub>3</sub> decomposition should be tightly related to  $PF_6^-$  group. Since no candidate exhibits the possibility to totally replace LiPF<sub>6</sub> in commercial system, the chemical decomposition of lithium carbonate seems unavoidable if it was directly exposed to electrolyte. The good understanding of its influence on cathode's performance should be helpful to construct the high quality cells. As  $Li_2CO_3$  is relatively easy to generate on surface of nickel rich content cathodes,  $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  was selected as the target to prepare  $Li_2CO_3$ -coated and LiF-coated samples in the following comparison.

In order to accelerate the Li<sub>2</sub>CO<sub>3</sub> generation rate, LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> sample was placed in glass dish and stored in desiccator with water at 55 °C for one month. The glass jar is opened daily to ensure the CO<sub>2</sub> content. As show in Fig. 3a & 3b, the signal of Li<sub>2</sub>CO<sub>3</sub> was detected with XRD and XPS after humidity corrosion. And TEM identifies this decomposing layer with a thickness of ~18 nm in Fig. 3g. It demonstrates that the sample after humidity corrosion is Li<sub>2</sub>CO<sub>3</sub>-coated LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>.



Figure 3 (a) XRD patterns and C1s (b) and F1s (c) XPS spectrum of fresh, Li<sub>2</sub>CO<sub>3</sub>-coated and LiF-coated LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> cathode material; SEM and HRTEM images of (d), (e) fresh, (f), (g) Li<sub>2</sub>CO<sub>3</sub>-coated and (h), (i) LiF-coated material

#### COMMUNICATION

According to the previous results, the Li<sub>2</sub>CO<sub>3</sub>-coated sample was mixed with electrolyte and heated at 80 °C for 12 h to prepare LiFcoated sample. As shown in Fig. 3a, Li<sub>2</sub>CO<sub>3</sub> is totally disappeared, and LiF becomes the only detectable impurity after this treatment. The weak broaden peak from 687.5 - 689.0 eV in Fig. 3c may be attributed to  $\text{Li}_x\text{PO}_y\text{F}_z$  during the heat process in electrolyte.<sup>25</sup> Combined with the TEM images (Fig. 3g, 3i), the dense Li<sub>2</sub>CO<sub>3</sub> layer changes to the porous LiF membrane. These results indicate that LiF-coated LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> was obtained after the electrolyte attack, which is consistent with the previous results.



 $\label{eq:schematic1} \begin{array}{l} \text{Schematic1} & \text{Surface reaction of } Li_2CO_3\text{-coated material in LiPF}_6 \\ electrolyte \end{array}$ 

The electrochemical performances of the as-synthesized,  $Li_2CO_3$ coated and LiF-coated  $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$  are compared in Fig. 4. The discharge capacity of the fresh sample is 192.5 mAhg<sup>-1</sup>. The discharge capacity of  $Li_2CO_3$ -coated sample was dropped to 170.5 mAhg<sup>-1</sup> (Fig. 4a). Since the discharge plateau is almost overlapped at the initial part, the lost capacity should be corresponding to the loss of active material instead of polarization. With this hypothesis, the decomposition ratio should be ~12%. After the electrolyte attack, sample capacity was recuperated to 174.2 mAhg<sup>-1</sup>. It is probably related to the relatively low molecule weight of lithium fluoride. Rate performance shares the same trend, as shown in Fig. 4b. The fresh,  $Li_2CO_3$ -coated and LiF-coated samples deliver 150.3, 124.1 and 132.0 mAhg<sup>-1</sup> at 5 C respectively.

All samples are cycled under 1C rate and their results are compared in Fig. 4c. The fresh material keeps 149.1 mAhg<sup>-1</sup>, 87.2% of the initial capacity after 200 cycling. The discharge capacity of Li<sub>2</sub>CO<sub>3</sub>-coated sample is seriously faded, only 37.1% retained after 200<sup>th</sup> cycle. In contrast, the LiF-coated sample still presents 143.5 mAhg<sup>-1</sup>, namely 91.9% of the initial discharge capacity, in the 200<sup>th</sup> cycle.

This improvement on cyclic stability for LiF-coated  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  should be related to the reaction of  $\text{Li}_2\text{CO}_3$  decomposition. According to the results in the former part, if it reacts inside of cell, the gaseous species of  $\text{Li}_2\text{CO}_3$  decomposition should be adsorbed on the surface of cathode material. Gas adsorption would decrease the active surface area and gradually aggregate the cell's polarization. The similar phenomenon is observed on zinc electrode, where the over-potential is quickly augmented by the H<sub>2</sub> absorption on Zn electrode.<sup>26,27</sup> As for LiF-coated sample, its interface between cathode and electrolyte is not interfered by the generated gas. Therefore it presents a stable cyclic stability.



**Figure 4** Electrochemical property of fresh,  $Li_2CO_3$ -coated and LiF-coated LiNi<sub>0.8</sub>CO<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> cathode material. (a) the discharge curves in first cycle at 0.1C; (b) rate capability at 0.1C, 0.2C, 0.5C, 1C, 2C and 5C; (c) cyclic stability tested at 1C.

#### Conclusion

The role of Li<sub>2</sub>CO<sub>3</sub> in LPF<sub>6</sub> electrolyte has been investigated in this work. Although it is electrochemically stable, Li<sub>2</sub>CO<sub>3</sub> could be chemically decomposed to LiF as the solid product, CO<sub>2</sub> & POF<sub>3</sub> as gaseous species. The generated gaseous species would be absorbed on cathode surface, aggregate the discharge polarization and deteriorate its cyclic stability. Obviously, if Li<sub>2</sub>CO<sub>3</sub> impurity was not able to well control in practical production, the treatment at high temperature to release the gas should be very helpful to keep the cell's cyclic stability.

#### Acknowledgements

We thank the 863 project (Grant No. 2013AA050906), the National Natural Science Foundation of China (Grant No. 51572273), Hundred Talents Program of the Chinese Academy of Sciences, Zhejiang Province Key Science and Technology Innovation Team (Grant No. 2013PT16), and Ningbo Natural Science Foundation (Grant No.2015A610250). Yujing Bi thanks the scholarship of International Joint PhD Training Program sponsored by University of Chinese Academy of Sciences.

Published on 02 February 2016. Downloaded by University of Connecticut on 02/02/2016 17:01:07

Journal Name

#### References

- 1 K. Xu, Chem. Rev., 2004, 104, 4303-4418.
- 2 S. Zhang, J. Power Sources, 2006, 162, 1379-1394.
- 3 J. Vetter, P. Novak, M. R. Wagner, C. Veit, K.-C. Moller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, *J. Power Sources*, 2005, **147**, 269-281.
- 4 D.-H. Cho, C.-H. Jo, W. Cho, Y.-J. Kim, H. Yashiro, Y.-K. Sun, S.-T. Myung, J. Electrochem. Soc., 2014, 161, A920-A926.
- 5 N. Tian, C. Hua, Z. Wang, L. Chen, J. Mater. Chem. A, 2015, 3, 14173-14177.
- 6 K. Xu, Chem. Rev., 2014, 114, 11503-11618.
- 7 H. Kobayashi, M. Shikano, S. Koike, H. Sakaebe, K. Tatsumi, J. Power Sources, 2007, **174**, 380-386.
- 8 M. Shikano, H. Kobayashi, S. Koike, H. Sakaebe, E. Ikenaga, K. Kobayashi, K. Tatsumi, J. Power Sources, 2007, 174, 795-799.
- 9 N. Takenaka, Y. Suzuki, H. Sakai, M. Nagaoka, J. Phys. Chem. C, 2014, 118, 10874-10882.
- 10 R. Wang, X. Yu, J. Bai, H. Li, X. Huang, L. Chen, X. Yang, J. Power Sources, 2012, 218, 113-118.
- 11 J. M. Garcia-Lastra, J. S. G. Myrdal, R. Christensen, K. S. Thygesen, T. Vegge, J. Phys. Chem. C, 2013, 117, 5568-5577.
- 12 C. Ling, R. Zhang, K. Takechi, F. Mizuno, J. Phys. Chem. C, 2014, 118, 26591-26598.
- 13 A. Manthiram, J. C. Knight, S.-T. Myung, S.-M. Oh, Y.-K. Sun, *Adv. Energy Mater.*, 2015, DOI: 10. 1002/aenm.201501010.
- 14 W. Liu, P. Oh, X. Liu, M.-J. Lee, W. Cho, S. Chae, Y. Kim, J. Cho, Angew. Chem. Int. Edit., 2015, 54, 4440-4458.
- 15 G. V. Zhuang, G. Chen, J. Shim, X. Song, P. N. Ross, T. J. Richardson, J. Power Sources, 2004, 134, 293-297.
- 16 Y. Bi, W. Yang, R., J. Zhou, M. Liu, Y. Liu, D. Wang, J. Power Sources, 2015, 283, 211-218.
- 17 R. Du, Y. Bi, W. Yang, Z. Peng, M. Liu, Y. Liu, B. Wu, B. Yang, F. Ding, D. Wang, *Ceram. Int.*, 2015, **41**, 7133-7139.
- 18 R. Petibon, L. Madec, D. W. Abarbanel, J. R. Dahn, J. Power Sources, 2015, 300, 419-429.
- 19 R. D. W. Kemmitt, D. R. Russell, D. W. A. Sharp, *Chem. Soc.*, 1963, 8, 4408-4413.
- 20 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. Rogers, *Green Chem.*, 2001, 3, 156-164.
- 21 L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Sci.*, 2015, **350**, 938-943.
- 22 A. W. Cresce, M. Gobet, O. Borodin, J. Peng, S. M. Russell, E. Wikner, A. Fu, L. Hu, H.-S. Lee, Z. Zhang, X.-Q Yang, S. Greenbaum, K. Amine, Kang Xu, J. Phys. Chem. C, 2015, 119, 27255-27264.
- 23 K. Xu, A. W. Cresce, J. Mater. Res., 2012, 27, 2327-2341.
- 24 A. W. Cresce, K. Xu, Electrochem. Solid State Lett., 2011, 14, A154.
- 25 L. Madec, J. Xia, R. Petibon, K. J. Nelson, J-P. Sun, I. G. Hill, J. R. Dahn, J. Phys. Chem. C, 2014, 118, 29608-29622.
- 26 J. W. Diggle, A. Damjanovic, J. Electrochem. Soc., 1972, 119, 1649-1658.
- 27 R. Barnard, J. Applied Electrochem., 1973, 3, 17-22.

## TOC



**RSC Advances Accepted Manuscript**