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The role of SnO_2 surface coating in the electrochemical performance of $Li_{1,2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ cathode materials



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HIGHLIGHTS

• The good conductive SnO_2 is used as the coating layer.

• SnO₂-coated cathode shows an improvement electrochemistry performance.

• The improved material shows the minimum amounts of transition metal dissolution.

• Ex-XRD patterns confirm that the improved material has a better layered structure.

• The coating layer plays an effective role in protecting the electrode from etching.

A R T I C L E I N F O

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ABSTRACT

The manganese metal ions and other transition metal ions in lithium manganite cathode materials will be dissolved into the electrolyte during cycling and storage at charged state, leading to severe capacity fading. Herein, the SnO₂-coated Li₁₂Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ cathode material is prepared successfully by a simple organic liquid-phase method. The data of inductive coupled plasma-atomic emission spectros-copy and ex-XRD suggest that the coating layer can effectively suppress the dissolution of metal ions, which maintains the stability of main structure. The value of the charge transfer impedance is 35.49 Ω cm² for LLMO-Sn1 after 50 cycles, while the LLMO is 123.30 Ω cm². The LLMO-Sn1 has the highest discharge capacity of 214.0 mAh·g⁻¹ after 150 cycles in half cell and exhibits the capacity retention of 86.8% after 150 cycles in full-cell. The decomposition reaction peak of LLMO-Sn1 appears at 250.1 °C.

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1. Introduction

Since the first commercialization of lithium-ion secondary battery by Sony Corporation in 1991, the lithium-ion secondary batteries have been widely used in our daily life. New demands are proposed for lithium-ion batteries to satisfy large scale equipment, such as higher energy density, lower price, etc. In this aspect, lithium-rich layered manganese based materials are very attractive, due to the high discharge capacity [1-3], low cobalt content, and high operating voltage.

Since layered Li₂MnO₃ (Li[Li_{1/3}Mn_{2/3}]O₂) and LiMO₂ have a similar structure, the lithium-rich layered manganese based materials can be described as $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Mn, Co, Ni, Fe, etc.) or lithium-rich layered solid solution Li[Li_xM_{1-x}]O₂ (M = Mn, Co, Ni, Fe, etc.), in which the Li₂MnO₃ compound is able to support the stability of the unit crystal cell [4]. Although the lithium-rich layered manganese based materials can deliver a high discharge capacity of more than 250 mAh·g⁻¹ at a high charging voltage (4.8 V, vs Li/Li⁺), it will undergo a large irreversible capacity loss (ICL) at first cycle, which is attributed to the extraction of the lithium as "Li₂O" from the Li₂MnO₃ compound with oxide ion vacancies elimination in the lattice [5,6]. The oxygen evolved from the Li₂MnO₃ compound has been demonstrated by Bruce et al. [7]



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directly in the *in-situ* differential electrochemical mass spectrometry. Furthermore, the catalytic side reaction between the electrolyte and the electrode surface can lead to an successive formation of a non-conducting solid electrolyte interface layer, which accelerate the structure transformation of cathode materials, resulting in the decrease of capacity [8,9]. In addition, the dissolution of manganese ions from cathode electrode, which is induced by the HF acid generated by fluorinated anions (PF_6^-) and protons [10], will also contribute a severe capacity fading [11] and a voltage fading [12].

Many efforts have been tried to improve the electrochemical performance of lithium-rich layered manganese based materials, such as surface modification [8,13-16], ions doping to replace transition metal ions [17], Li⁺ ions [18] and oxygen ions in the materials [19]. Among these efforts, the surface modification has been proved to be an effective way to enhance the stability of electrolyte/electrode interface and improve the electrochemical performance of lithium-rich layered manganese based materials. SnO₂ with a good electronic conductibility has been used as a coating layer to improve the electrochemical performance of LiCoO₂ [20], LiFePO₄ [21], and LiMn_{1.5}Ni_{0.5}O₄ [22]. Zhu et al. [16] has reported the lithium-rich layered manganese based materials with a $SnO_{2-x}F_x$ coating layer showed an excellent cyclability. However, the pure SnO₂ phase as the coating layer has not been systematically investigated. Meanwhile, the introduction of fluorine increases the complexity of operation.

In this paper, a good conductive SnO_2 coating layer is formed on the surface of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$ (LLMO) by an organic liquid phase method. The surface modified material shows an excellent long-life cycling and good rate performance. Even in the full-cell (LLMO/graphite) tests, the material with SnO_2 coating layer (LLMO-Sn1) also exhibit a good cycle retention rate. The data of inductive coupled plasma-atomic emission spectroscopy (ICP-AES) confirm that the coating layer is quite effective in inhibiting the dissolution of transition metal ions, especially for the manganese and nickel ions. Thus, the degradation of the cathode is suppressed, to improve the stability of cathode material. The data of ex-X-ray diffraction indicate the LLMO-Sn1 sample has a better layered structure after 100 cycles at 1C rate.

2. Experiment

Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ cathode materials were synthesized by liquid-phase method [23]. Stoichiometric amounts of а MnSO₄·4H₂O (>99.0%, AR, Sinopharm Chemical Reagent Co. Ltd), $CoSO_4 \cdot 7H_2O$ ($\geq 99.0\%$, AR, Sinopharm Chemical Reagent Co. Ltd), NiSO₄· $6H_2O$ (\geq 99.0%, AR, Sinopharm Chemical Reagent Co. Ltd) were dissolved into 150 ml deionized water. 50 ml ethanol (AR, Sinopharm Chemical Reagent Co. Ltd) was added into the mixed metal salt solution. After stirred 1 h, the 200 ml NH₄HCO₃(AR, Sinopharm Chemical Reagent Co. Ltd) solution was dropped into the mixed metal salt solution to form a suspension. The powder was collected through filtration after 1 h at 10 °C, then dried in a vacuum oven at 80 °C. The obtained powder was heated at 500 °C for 5 h and obtained a black powder. The black powder mixed well with LiOH \cdot H₂O (3 wt% excess, \geq 95.0%, AR, Sinopharm Chemical Reagent Co. Ltd) was calcined at 480 °C for 4 h and at 800 °C for 12 h in air. The final material was Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂, which was denoted as LLMO. The heating rate was 5 °C min⁻

Adequate amount of $SnCl_4 \cdot 5H_2O$ ($\geq 99.995\%$, metals basis, Aladdin) was dissolved into a 200 ml ethanol, then, 0.5 g LLMO powder was added. After ultrasonically treated for 1 h, the NH₃·H₂O (GR, Sinopharm Chemical Reagent Co. Ltd) solution was added to form a precipitate. After a centrifuging process, the precipitation was heated at 500 °C for 5 h in air, resulting in LLMO-Sn. According to the weight ratios of SnO₂/LLMO, two samples were synthesized, which were named as LLMO-Sn1 (1 wt% SnO₂) and LLMO-Sn3 (3 wt% SnO₂) (Table 1), respectively. The pure SnO₂ was also prepared in this way without adding the LLMO powders. All the reagents have not been further purified.

The Rigaku Ultima IV (Rigaku Corporation) using Cu-K α radiation was used to determine the crystal structures of all materials. The data were collected in the range of 2 theta values between 10° and 90° at an interval of 0.02° and then analyzed using PDXL-2 analysis software. The S-4800 (Hitachi Corporation) was used to determine the morphologies of all materials. Elemental mappings of all materials were carried out on the energy dispersive X-ray detector (EDX, the accessory of S-4800). Transmission electron microscopies (TEM) were performed on the JEM-2100 (JEOL). The inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine the elemental compositions of materials.

Electrochemical performances of materials in this paper were tested through the CR2032-type coin cells. The 1.0 M LiPF₆ in mixed organic solution of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (1:1:1, volume ratio) was used as the electrolyte. Celgard 2400 was used as the separator to separate the positive and negative electrodes. The slurry was composed of the active material, acetylene and polyvinylidene fluoride (PVDF) with the weight ratio of 8:1:1 in *N*-methyl-2-pyrrolidone (NMP). The slurry was coated onto the aluminum foil to get the electrode sheet. The electrode sheet was dried at 80 °C in vacuum for overnight. All the coin cells were assembled in the Arfilled glovebox (Mbraun, Germany). Each of the active materials for all cells was controlled at about 2.5 mg. In the half-cell, the lithium metal foil was the anode, while in the full-cell, the graphite (Rightful Technology Co. Ltd, China) served as the anode.

The charge/discharge tests were carried out galvanostatically on a Land CT2001A (Wuhan, China) battery testing system at 25 °C between 2.0 V–4.8 V. For charge/discharge cycling performances, the current of 125 mA g⁻¹ was used as 0.5 C. The rate performances were carried out at rates ranging from 0.1 C to 5 C. The electrochemical performances of full-cells were performed at rate of 0.1 C between 1.95 V–4.75 V.

The thermal stability of electrode in the electrolyte mentioned above was measured by the DSC/TG (STA 449 F3 Jupiter Netzsch) from 100 °C to 300 °C. Details of the treatment are described as follows: 1) cells were cycled for one circle at the rate of 0.1 C, and then charged to 4.8 V, held for 2 h; 2) cells were disassembled in an Ar-filled glove box to get charged cathode films; 3) the films were respectively immersed and washed in the DMC and naturally dried in the glove box; 4) the electrode materials stripped from the cathode and the electrolyte were respectively put into in a stainless steel crucible at the ratio of 10 μ L electrolyte per 1 mg electrode material.

In the full-cell, the deposition amount of metal ions on the anode was calculated by ICP-AES. Firstly, full-cells were cycled for 50 circles at 0.5C rate between 1.95 V–4.75 V, and then discharged to 1.95 V at the 50th circle. Secondly, all full-cells were disassembled to obtain the anode, the separator and the cell cases. All of these were rinsed by deionized water. All of them were respectively put into a 25 ml color comparison tube containing 6 M HCl water solution. The solution was tested by ICP-AES, obtaining the dissolution amount of transition metal ions.

Table 1			
The gram of S	nCl ₄ ·5H ₂ O use	d for the coa	ting purpose.

Sample name	Amount of SnCl ₄ ·5H ₂ O/g	Amount of LLMO/g
LLMO-Sn1	0.0116	0.5
LLMO-Sn3	0.0349	0.5

3. Results and discussion

X-ray diffraction (XRD) pattern of SnO₂ are shown in Fig. 1a. All diffraction peaks are attributed to a rutile structure of SnO₂ (space group: P4₂/mnm-136, JCPDS no.01-077-0447) without impurity, which indicates that pure SnO₂ material has been prepared in this paper. The XRD patterns of LLMO. LLMO-Sn1. and LLMO-Sn3 are exhibited in Fig. 1b. The main diffraction peaks of LLMO sample can be indexed as the layered α -NaFeO₂ structure, except some weak peaks between 20° and 25° that are associated with the Li⁺ and Mn^{4+} ordering arrangement in the transition metal layers [24]. Compared to the LLMO sample, there are no extra diffraction peaks in the LLMO-Sn1 and LLMO-Sn3 samples. Meantime, the obvious splits located in (016)/(012) and (018)/(110) diffraction peaks suggest that both the materials are of good layered structures in lattices. The reason may be that the content of SnO₂ in LLMO-Sn1 and LLMO-Sn3 is very low, as others have reported [20-22]. The XRD data can suggest that the surface modification does not change the structure of pristine material.

Scanning electronic microscopy (SEM) images of all samples are shown in Fig. 2. There is no significant difference among LLMO, LLMO-Sn1 and LLMO-Sn3. The EDS result of the red square marked on SEM images (the insert image in Fig. 2b) shows the existence of Sn element on the surface. To further confirm the existence of SnO₂ on the surface, the high resolution transmission electron microscopy (HRTEM) was carried out (Fig. 3). The spacing of the lattice fringes measured for the LLMO and LLMO-Sn1 were both about 0.47 nm, corresponding to the interplanar distance of (003) planes of the layered structure [25]. There are significant differences in electron diffraction patterns between the LLMO and LLMO-Sn1. The spacing of the lattice fringes for the outer layer is 0.47 nm,



Fig. 1. XRD patterns: (a) pure SnO₂, (b) LLMO, LLMO-Sn1 and LLMO-Sn3.

corresponding to the interplanar distance of the (100) planes of the cubic structure SnO_2 (space group: $P4_2$ /mnm-136) [26], while the internal spacing lattice fringes corresponds to the d-spacing of the (003) planes of the layered structure (rhombohedral structure). It is determined that the SnO_2 coating layer has been formed on the surface of the LLMO material.

The first charge/discharge cycle performances at 0.1 C of LLMO. LLMO-Sn1 and LLMO-Sn3 are shown in Fig. 4a. The similar charge/ discharge curves can be seen on all the three samples. The charge curve can be divided into two portions. In the slope part below 4.5 V, the oxidation reaction is associated with the Ni^{2+} to Ni^{4+} and Co^{3+} to Co^{4+} , while in the prolonged plateau part, the reaction is ascribed to the transition metal ion rearrangements accompanying the loss of oxygen [27]. It is noted that the LLMO-Sn1 and LLMO-Sn3 show reduced charge capacities, while the LLMO-Sn1 can deliver the highest discharge capacity among them. The reason may be that the side reactions between the cathode surface and the electrolyte are suppressed by the coating layer. Furthermore, the coating layer could provide more oxygen ion vacancies in the layered lattice to accommodate more Li⁺ ions [28]. The LLMO sample shows the coulomb efficiency of 71.6%, while that of the LLMO-Sn1 is 82.4%. The values of the irreversible capacity loss in the first charge/discharge cycle for LLMO, LLMO-Sn1 and LLMO-Sn3 is 99.5 mAh \cdot g⁻¹, 55.3 mAh \cdot g⁻¹, and 54.0 mAh \cdot g⁻¹, respectively. It is can be seen that the values of irreversible capacity loss decrease after the SnO₂ coating, just as others have reported [29–31]. Fig. 4b shows the cycle performances of all samples at the current density of 125 mA·g⁻¹ between 2.0 V–4.8 V. The LLMO-Sn1 has the highest discharge capacity of 214.0 mAh \cdot g⁻¹ after 150 cycles, while the LLMO-Sn3 shows the discharge capacity of 182.1 mAh \cdot g⁻¹. Both of SnO₂ coating samples show obvious improvements on the cycling stability. The reason might be that the coating layer can suppress the side reactions and protect the surface structure of bulk material [8,13-16].

The effect of coating layer on the rate capability performance of active material is shown in Fig. 4c. The discharge capacity of all samples was tested at rates ranging from 0.1 C to 5 C, meanwhile the value of current density during the charge process is the same as the discharge process. At high C rate, such as 5 C, the LLMO-Sn1 can deliver the discharge capacity of 130.0 mAh·g⁻¹, while the LLMO only delivers 110 mAh·g⁻¹. The LLMO-Sn1 shows a higher discharge capacity at the rates ranging from 0.1 C to 5 C. In order to further discuss the influence of coating layer on the Li⁺ ions transmission, EIS has been carried out as shown in Fig. 5.

EIS is usually used to analyze the transport and kinetics of Li⁺ ions in electrolyte, and charge transfer across the electrolyte/electrode interface [32]. The half-cells were cycled at 25 mA \cdot g⁻¹ for one cycle and then cycled at 250 mA \cdot g⁻¹ for 50 cycles. The half-cells were respectively charged to 4.8 V at the 2nd lap and the 50th laps (Fig. 5). All the Nyquist plots curves resemble each other. In high frequency, the small semicircle corresponds to the impedance (R_s) of Li⁺ diffusion through the surface interface. In the medium frequency, the semicircle corresponds to the charge transfer impedance (R_{ct}) of Li⁺ diffusion through the electrolyte/electrode interface [33]. In order to facilitate discussing the influences of coating layer on the Li⁺ ions diffusion, the EIS spectra are fitted to an equivalent circuit. As the cycling goes on, the R_{ct} for LLMO sample increases from 14.15 Ω cm² to 123.30 Ω cm², however, the R_{ct} for LLMO-Sn1 sample increases from 15.57 Ω cm² to 35.49 Ω cm². After 50 cycles, the R_{ct} of LLMO-Sn1 sample is much smaller than that of LLMO sample. It indicates that the coating layer can protect the surface structure of bulk material and suppress the side reactions. Furthermore, whatever the SnO_2 or the $SnO_{2-x}F_x$, product of SnO₂ etched by the HF acid, both of them have good electronic conductivity, which can reduce the R_{ct}.



Fig. 2. SEM images: (a) LLMO, (b) LLMO-Sn1, (selected EDS element mappings, below right), (c) LLMO-Sn3.



Fig. 3. TEM images: (a) LLMO, (b) LLMO-Sn1; HRTEM images: (c) LLMO, (d) LLMO-Sn1.



Fig. 4. (a) The first charge/discharge curves, (b) cycle performances and (c) rate performances of the cells with different cathode materials.



Fig. 5. Nyquist plots of LLMO (a), LLMO-Sn1 (b) electrodes after the 2nd cycle and the 50th cycle at the charge state of 4.8 V and the rate of 1 C.

It is well-known that in the lithium-rich layered manganese based materials, the active Li_2MnO_3 (Mn^{4+} to Mn^{3+}) compound can provide an additional capacity. However, due to the Jahn-Taller effect and the corrosion of HF, the manganese metal ions and other transition metal ions will be dissolved into the electrolyte, leading to severe capacity fading in lithium manganate-carbon cells [11]. In order to investigate the protective effects of coating layer on the active cathode electrode, the full-cells were assembled. Fig. 6a shows the charge/discharge cycle of the full-cell with the LLMO-Sn1 cathode and the graphite anode during the initial two cycles. Based on the weights of cathode active materials, the fullcells are cycled between 1.95 V and 4.75 V at the rate of 0.1 C. The coulombic efficiencies of the full-cells at the first cycle are all lower than the half-cells. It maybe results from the solid electrolyte interface (SEI) generation on the graphite anode [34]. However, the full-cell of LLMO-Sn1 still exhibits the capacity retention of 86.8% after 150 cycles (Fig. 6b).

All the full-cells were respectively disassembled to determine

the amount of transition metal dissolution, shown in Fig. 7. The weight percentage was calculated according to the following formula:

$$\mathbf{w}.\% = (\mathbf{W}1 \div \mathbf{W}0) \times 100\% \tag{1}$$

The weight percentage was defined as w.%. The weights of transition metal dissolutions (W1) were measured by ICP-AES, and the weight of active cathode materials (W0) does not include the mass of the surface coating layer. As shown in Fig. 7, it is noted that a significant difference between the LLMO-Sn1 sample and LLMO sample. The dissolution of transition metal is significantly lower in LLMO-Sn1 sample, owing to the protection provided by the coating layer. The surface structure of bulk material will be destroyed by the transition metal dissolution, resulting in blocking the Li⁺ ion transport. This result can well explain why the LLMO sample has a higher impedance in the EIS tests. Correspondingly, certain amounts of manganese, cobalt, and nickel were dissolved from the LLMO electrode material. The transition dissolution is mainly due to



Fig. 6. (a) First charge/discharge curves of LLMO-Sn1/graphite, (b) cycle performance of LLMO-Sn1/graphite, (c) cycle performance of LLMO/graphite.



Fig. 7. (a) Dissolution histogram of metal ions, (b) Ex-XRD patterns of LLMO and LLMO-Sn1.

the following reasons:

(1) The Mn³⁺ at the surface may be dissolved into the electrolyte, due to the following chemical reaction equation [35]:

$$2Mn^{3+}_{solid} \rightarrow Mn^{4+}_{solid} + Mn^{2+}_{solution}$$

- (2) In organic solvents, the highly-delithiated particles are not stable at the end of charge, for example, the high oxidation ability of Mn⁴⁺ [36] will lead to decomposition of solvents.
- (3) The electrode would be attacked by HF due to the reaction between LiPF₆ and protons, resulting in the structural instability [37,38].

It has been reported that the surface modification on cathode materials can decrease the transition metal dissolution [36,39]. According to the ex-XRD data (Fig. 7b), the LLMO-Sn1 sample show a better layer structure than the LLMO sample. This can explain why the LLMO-Sn1 shows a superior long life cycle performance in the half-cell tests.

Safety is the paramount concern for lithium-ion batteries, and a good thermal stability of the cathode material in charged state is crucial to improve reliability. DSC curves of LLMO and LLMO-Sn1 electrode materials were respectively measured at 4.8 V after the 10th cycle at 0.5 C, shown in Fig. 8. The area of the exothermic peak reveals the amount of heat released, which is generated from the decomposition of oxides and the reactions between the cathode and electrolyte [40]. For the LLMO, the decomposition reaction peak appears at 238.2 °C. On the other hand, the LLMO-Sn1 shows



Fig. 8. DSC curves of LLMO and LLMO-Sn1 at 4.8 V charged state.

not only the higher peak temperature of 250.1 °C, but also the lower level of heat generation. It is obvious that the thermal stability is improved by SnO_2 coating modification. The results may indicate that the crystallized SnO_2 coating layer can positively suppress the side reactions between the active electrode and electrolyte, and reduce the exothermic reactions. Another possible reason for the improved thermal stability may be that the coating layer introduces strong Sn-O bond onto the surface to decrease the oxygen activity, protect the surface of active material electrode and suppress the generation of oxygen.

4. Conclusion

In conclusion, the SnO₂-coated Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ cathode material was prepared successfully by a simple organic liquidphase method. The fundamental functions of SnO₂ coating layer are summarized below. Firstly, the SnO₂ coating layer can separate the highly-delithiated active electrode material from the electrolyte, reducing the decomposition of the electrolyte with low transfer impedance. Secondly, the SnO₂ coating layer can greatly reduce the migration of transition metal ions from the active electrode to the electrolyte and anode since the layer can resist the attack of HF. At last, the structural stability of electrode material is enhanced, leading to the lower interface impedance, better thermal stability, and better full-cell performance. The material with SnO₂ surface modification has the high discharge capacity of 259.5 mAh g^{-1} with the coulomb efficiency of 82.3% in the first charge/discharge cycle under the current of 25 mA \cdot g⁻¹ in the half-cell. After 150 cycles under the current of 250 mA \cdot g⁻¹, the surface modified material still can deliver the discharge capacity of 214.0 mAh \cdot g⁻¹ in the half-cell. The coated SnO₂ layer plays an effective role in protecting the cathode from etching caused by the acidic substances in the electrolyte, to improve the stability of electrode material. Thus, an improved long-life cycling performance of the cathode is obtained.

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References

- [1] H.J. Kim, H.G. Jung, B. Scrosati, Y.K. Sun, J. Power Sources 203 (2012) 115-120.
- [2] J.L. Liu, L. Chen, M.Y. Hou, F. Wang, R.C. Che, Y.Y. Xia, J. Mater. Chem. 22 (2012) 25380.
- [3] Y. Wang, N. Sharma, D. Su, D. Bishop, H. Ahn, G. Wang, Solid State Ion. 233

(2013) 12 - 19.

- [4] H. Yu, R. Ishikawa, Y.G. So, N. Shibata, T. Kudo, H. Zhou, Y. Ikuhara, Angew. Chemie Int. Ed. Engl. 52 (2013) 5969–5973.
- [5] D. Ye, K. Ozawa, B. Wang, D. Hulicova-Jurcakova, J. Zou, C. Sun, L. Wang, Nano Energy 6 (2014) 92–102.
- [6] F. Dogan, B.R. Long, J.R. Croy, K.G. Gallagher, H. Iddir, J.T. Russell,
- M. Balasubramanian, B. Key, J. Am. Chem. Soc. 137 (2015) 2328–2335.
 [7] A.R. Armstrong, M. Holzapfe, S.H. Kang, M.M. Thackeray, P.G. Bruce, J. Am. Chem. Soc. 128 (2006) 8694-8698.
- [8] W. Liu, P. Oh, X. Liu, S. Myeong, W. Cho, J. Cho, Adv. Energy Mater. 13 (2015) 1500274-1500285.
- [9] Z. Wang, E. Liu, C. He, C. Shi, J. Li, N. Zhao, J. Power. Sources 236 (2013) 25-32.
- [10] G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Gozdz, D. Larcher, I.M. Tarascon, J. Power Sources 69 (1997) 11–25.
- [11] C. Zhan, J. Lu, A.J. Kropf, T.P. Wu, A.N. Jansen, Y.K. Sun, X.P. Qiu, K. Amine, Nat. Commun. 4 (2013) 3437–3445.
- [12] J. Zheng, M. Gu, J. Xiao, P. Zuo, C. Wang, J.G. Zhang, Nano Lett. 13 (2013) 3824-3830.
- [13] J. Zheng, M. Gu, J. Xiao, B.J. Polzin, P. Yan, X. Chen, C. Wang, J.-G. Zhang, Chem. Mater. 26 (2014) 6320-6327.
- [14] E. Zhao, X. Liu, Z. Hu, L. Sun, X. Xiao, J. Power Sources 294 (2015) 141–149. [15] H.J. Lee, Y.J. Park, J. Power Sources 244 (2013) 222-233.
- [16] X. Zhu, Y. Wang, K. Shang, W. He, X. Ai, H. Yang, Y. Cao, J. Mater Chem. A 3
- (2015) 17113-17119.
- [17] Y. Wang, Z. Yang, Y. Qian, L. Gu, H. Zhou, Adv. Mater. 27 (2015) 3915–3920.
 [18] K. Du, F. Yang, G.R. Hu, Z.D. Peng, Y.B. Cao, K.S. Ryu, J. Power Sources 244 (2013) 20-29.
- [19] H.Z. Zhang, Q.Q. Qiao, G.R. Li, X.P. Gao, J. Mater Chem. A 2 (2014) 7454-7460.
- [20] C. Hudaya, J.H. Park, J.K. Lee, W. Choi, Solid State Ion. 256 (2014) 89–92.
- [21] D. Ziolkowska, K.P. Korona, B. Hamankiewicz, S.-H. Wu, M.-S. Chen, J.B. Jasinski, M. Kaminska, A. Czerwinski, Electrochimica Acta 108 (2013)

532-539.

- [22] Y. Lee, T.Y. Kim, D.W. Kim, J.K. Lee, W. Choi, J. Electroanal. Chem. 736 (2015) 16-21.
- [23] B. Li, Y.Y. Yu, J.B. Zhao, J. Power Sources 275 (2015) 64–72.
 [24] M.M. Thackeray, S.H. Kang, C.S. Johnson, J.T. Vaughey, R. Benedek, S.A. Hackney, J. Mater. Chem. 17 (2007) 3112–3125.
- [25] M.M. Thackeray, S.H. Kang, C.S. Johnson, J.T. Vaughey, S.A. Hackney, Electrochem. Commun. 8 (2006) 1531–1538.
- [26] J.Q. Hu, Y. Bando, Q.L. Liu, D. Golberg, Adv. Funct. Mater. 13 (2003) 493–496.
 [27] C.S. Johnson, J.S. Kim, C. Lefief, N. Li, J.T. Vaughey, M.M. Thackeray, Electro-
- chem. Commun. 6 (2004) 1085–1091.
- [28] Y. Wu, A. Manthiram, Solid State Ion. 180 (2009) 50-56.
- [29] J.M. Zheng, J. Li, Z.R. Zhang, X.J. Guo, Y. Yang, Solid State Ion. 179 (2008) 1794-1799
- [30] S.J. Shi, J.P. Tu, Y.Y. Tang, X.Y. Liu, Y.Q. Zhang, X.L. Wang, C.D. Gu, Electrochimica Acta 88 (2013) 671–679.
- [31] M. Xu, Z. Chen, L. Li, H. Zhu, Q. Zhao, L. Xu, N. Peng, L. Gong, J. Power Sources 281 (2015) 444-454.
- [32] S.J. Shi, J.P. Tu, Y.Y. Tang, X.Y. Liu, X.Y. Zhao, X.L. Wang, C.D. Gu, J. Power Sources 241 (2013) 186–195.
- [33] J. Liu, B. Reeja-Jayan, A. Manthiram, J. Phys. Chem. C 114 (2010) 9528-9533.
- K. Edstrom, M. Herstedt, D.P. Abraham, J. Power Sources 153 (2006) 380-384. [34]
- [35] M. Chi, C. Fell, B. Xu, S. Meng, Microsc. Microanal. 17 (2011) 1574–1575.
- [36] C. Li, H.P. Zhang, LJ. Fu, H. Liu, Y.P. Wu, E. Ram, R. Holze, H.Q. Wu, Electro-chimica Acta 51 (2006) 3872–3883.
- [37] Y.K. Sun, J.M. Han, S.T. Myung, S.W. Lee, K. Amine, Electrochem. Commun. 8 (2006) 821-826.
- [38] K. Amine, J. Liu, S. Kang, I. Belharouak, Y. Hyung, D. Vissers, G. Henriksen, J. Power Sources 129 (2004) 14-19.
- [39] J.G. Li, L. Wang, Q. Zhang, X.M. He, J. Power Sources 190 (2009) 149-153.
- [40] W. Chang, J.W. Choi, J.C. Im, J.K. Lee, J. Power Sources 195 (2010) 320-326.