

A High-Performance Sodium-Ion Full Cell with a Layered Oxide Cathode and a Phosphorous-Based Composite Anode

Seung-Min Oh, Pilgun Oh, Sang-Ok Kim,* and Arumugam Manthiram**,^z

Materials Science and Engineering Program & Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, USA

A low-cost sodium-ion full cell with a O3-type layered Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ cathode and an alloy-type P-TiP₂-C anode is presented. The cathode is synthesized by an oxalate coprecipitation method and optimized cathodes shows a high specific capacity of 135 mAh g⁻¹ at 0.1C rate with a high rate capability of 90 mAh g⁻¹ at 1C rate and 70 mAh g⁻¹ at 2C rate with good cyclability. The full cell exhibits better capacity retention than the half cell with the cathode due to the elimination of the degradation caused by sodium-metal anode. The dramatically enhanced electrochemical performance of the Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ / P-TiP₂-C full cell compared to that of the sample with no Cu is attributed to the structural stabilization imparted by Cu by suppressing the phase change from the O3 structure to the P3 structure during cycling.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0931702jes] All rights reserved.

Manuscript submitted October 17, 2016; revised manuscript received December 12, 2016. Published December 29, 2016.

As the demand for rechargeable batteries is increasing, the research activities in the Li-ion battery area had grown exponentially during the past 25 years.^{1,2} However, due to the relatively low abundance of lithium resources and the high cost, there is immense interest to develop battery chemistries based on low-cost working ions, particularly for large-scale applications. In this regard, Na-ion batteries are emerging as an alternative due to the high abundance and low cost of Na. In addition, the larger size of Na⁺ compared to Li⁺ helps to minimize the cation disorder between Na⁺ and the transition-metal ions. Therefore, various kinds of Na-based cathode materials have been investigated with the O3-type layered,³⁻¹⁹ P2-type layered,²¹⁻²⁹ and polyanion-type structures.³⁰⁻³² Among them, the O3-type cathode materials are the most promising due to their similarity to the well-known LiCoO2 cathode used in lithium-ion industry. Also, as has been reported in the literature, the O3-type cathodes have much more stable crystal structure and capacity retention than the P2-type cathode materials.^{7,18,19}

With the above perspective, several O3 type cathode compositions have been introduced, but they are generally based on expensive transition metal ions such as Ni and Co.7,8,10-15,17 To take the low-cost advantage of sodium-ion batteries, it is critical to replace these expansive transition-metal ions by low-cost transition-metal ions such as Fe, Mn and Cu. In this regard, several research groups have focused on the Fe-based O3-type cathode NaFeO₂.^{4–6} However, the high-spin Fe³⁺: $t_{2g}^{3}e_{g}^{2}$ ions tend to migrate readily from the octahedral sites in the transition-metal layer to the octahedral sites in the sodium layer via a neighboring tetrahedral site as the Fe³⁺ ion has no particular preference for octahedral sites.⁴ Therefore, to overcome this difficulty, it is necessary to mix Fe with other transition-metal ions such as in Na(Fe,Co)O₂, Na(Ni,Fe,Mn)O₂, and Na(Fe,Mn)O₂.^{8,10,11,17,18,35} Through this approach, the Fe migration problem has been suppressed to some extent. Nevertheless, the use of expensive Co or Ni in those compositions still works against the low-cost proposition of Na-ion battery systems. Recently, Mu et al. reported the Cu-containing O3type cathode $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$, displaying 98 mAh g⁻¹ at 0.1 C-rate. This material was synthesized by a solid-state reaction that yielded a particle size of $10-30 \,\mu m^{20}$

Despite an intensive investigation of cathode and anode hosts for sodium-ion cells in recent years, full cell data with optimized cathode and anode compositions and optimized particle size or morphology are rarely available in the literature. Accordingly, we present here the synthesis of Na[(Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]O₂ with $0 \le x \le 0.2$ by an oxalate method and their physicochemical and electrochemical characterization. Then, an optimized cathode composition with x

= 0.2 is assembled into a full cell with a phosphorous-based alloytype anode P-TiP₂-C developed in our group. The assembled full cell Na[(Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ / P-TiP₂-C exhibits better performance than the half-cell with the Na[(Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ cathode due to the elimination of the degradation caused by sodium-metal anode during cycling.

Experimental

Material synthesis.—The $[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]C_2O_4$ (x = 0, 0.1, and 0.2) precursors were synthesized via a co-precipitation method. $Cu(NO_3)_2\cdot 6H_2O,\ FeSO_4\cdot 7H_2O,\ MnSO_4\cdot H_2O,\ (NH_4)_2C_2O_4,\ and$ H₂C₂O₄ were employed as the starting materials. To synthesize the $(Fe_{1/3}Mn_{2/3})C_2O_4 \cdot H_2O$ precursor, stoichiometric amounts of $FeSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot H_2O$ were dissolved in distilled water to a concentration of 0.5 mol dm⁻³. This metal solution was then dropped into a continuously stirring solution of ammonium oxalate. At the same time, an appropriate amount of NH₄OH solution was added into the beaker to adjust the pH value to 5. The concentration of the solution, pH, temperature, and stirring speed were carefully controlled. The co-precipitation solution was continuously stirred for 3 h while keeping the temperature constant at 70°C. CuC_2O_4 was synthesized using $Cu(NO_3)_2\cdot 6H_2O$ and $H_2C_2O_4$ with the same method described above. After the reaction, the precursor powders were filtered, washed, and dried in a vacuum oven overnight at 110°C. The Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]C₂O₄ (x = 0, 0.1, and 0.2) samples were prepared by thoroughly mixing the precursors (Fe_{1/3}Mn_{2/3})C₂O₄ and CuC₂O₄ with Na₂CO₃, heating at 900°C in air for 15 h with a heating rate 3°C min⁻¹, and quenching the sample to room temperature.

Physical properties.—The synthesized samples were characterized with powder X-ray diffraction (XRD, MiniFlex 600, Rigaku) using Cu-K α radiation. Particle morphologies of the precursor and the as-synthesized powders were observed by scanning electron microscopy (SEM, Quanta 650 ESEM, FEI) equipped with energy dispersive spectroscopic (EDS) analysis. Chemical compositions of the prepared powder were analyzed with an inductively-coupled plasmaoptical emission spectroscopy (ICP-OES). The oxidation state of each ion in the samples was investigated with X-ray photoelectron spectroscopy (XPS, Kratos Analytical). High resolution transmission electron microscopy (TEM: JEOL 2010F) was used to analyze the surface morphology and crystal structure of the powder samples.

Electrochemical properties.—Electrochemical testing was performed with 2032R coin-type cells using Na metal (Alfa Aesar., USA) as an anode. The cathodes were fabricated by blending the prepared Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]C₂O₄ (x = 0, 0.1, and 0.2) powders (85 wt%), carbon black (7.5 wt%), and polyvinylidene fluoride (7.5 wt%) in *N*-

^{*}Electrochemical Society Student Member.

^{**}Electrochemical Society Fellow.

^zE-mail: manth@austin.utexas.edu



Figure 1. (a) SEM images and (b) XRD patterns of $Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]O_2$ (x = 0, 0.1, and 0.2). (c) Schematic crystal structures of the samples with x = 0 and 0.2.

methylpyrrolidinone. The slurry was then cast onto an aluminum foil and dried at 110°C for 12 h in a vacuum oven, and then disks were punched out of the foil. The electrolyte solution was 1.0 M NaClO₄ in a 98:2 by volume mixture of propylene carbonate and fluoroethylne carbonate (Aldrich). The electrolytes were carefully used inside an Ar-filled dry box due to the air sensitivity of the NaClO₄ salt. The active material loading in the cathode and anode were, respectively, 2 and 0.5 mg cm⁻², with corresponding electrode thicknesses of 40 μ m and 15 μ m. All cells were prepared in an Ar-filled dry box. The half cells were cycled in a constant current mode at a 0.1C rate in the voltage range of 1.2–4.3 V versus Na (where 1C = 120 mAh g⁻¹). For full cell test, P-TiP₂-C was used as an anode. The negative and positive electrode capacity ratio for full cell (N/P ratio) was 1.3.

Results and Discussion

Determination of the chemical composition of the final products by the inductively coupled plasma analysis (ICP) confirmed that the final compositions were in agreement with the designed compositions (see Table S1). Figures 1a-c shows that the morphologies and crystal structures of the synthesized samples. As seen in Figure 1a, all materials are round-shaped with a particle size of $2 - 3 \mu m$. No morphological differences were found from the SEM results with Cu content. The X-ray diffraction (XRD) patterns of the Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]O₂ (x = 0, 0.1, and 0.2) samples reveal that all samples have the well-crystalized O3-type rhombohedral structure with the R-3m space group. The lattice parameters of these samples calculated with the least squares method are given in Table S2 (see supplementary material). Interestingly, the main peaks that are around $2\Theta = 30$ to 40° are shifted to lower angle with increasing Cu content due to an increase in the lattice parameters caused by a larger ionic radius of Cu^{2+} (0.73 Å) compared to those of Fe^{3+} (0.645 Å), Mn^{3+} (0.645 Å), and Mn^{4+} (0.53 Å).

We also recorded the SEM images and the EDS elemental mapping of the Na[Fe_{1/3}Mn_{2/3}]O₂ and Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3}]O₂ powders. As seen in Figure 2a, the Na[Fe_{1/3}Mn_{2/3}]O₂ sample with no Cu shows a uniform distribution of Na, Mn, and Fe. Similarly, the Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ sample exhibits a uniform distribution of Na, Mn, Fe, and Cu (Figure 2b).

The electrochemical performances of the samples were assessed with coin type half cells assembled with Na metal as the anode. To optimize the charge cutoff voltage, we tested the cells with different voltage ranges as shown in Figure S4 (1.2 - 4.3 V and 1.2-4.4 V). However, the gain in capacity on increasing the cutoff voltage to 4.4 V was not significant, so we decided to keep the cutoff voltage at 4.3 V to avoid aggravated electrolyte decomposition at higher voltages. For the charge-discharge tests, therefore, all cells were charged to 4.3 V and then discharged to 1.2 V at a constant current of 0.1C rate at room temperature. As the Cu content increases, the specific capacity in the first cycle increases dramatically (Figure 3a). The Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]O₂ sample with x = 0.2 shows the highest discharge capacity of 135 mAh g^{-1} at 0.1C rate in the first cycle and the x = 0 sample shows the lowest discharge capacity of 60 mAh g⁻¹ at the same rate and cycle. We also compared the specific capacity and synthetic condition of the $Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O_2$ sample with other Fe-containing materials in the literature as in Table S3. From this comparison, we concluded that our synthetic method is effective to make layered materials for sodium-ion battery.

The enhanced discharge capacity of the Cu-containing samples is due to (i) the decreased amount of Fe in the sample and suppression Fe migration to the Na sites during cycling due to Cu substitution and (ii) the higher electrochemical activity of the substituted Cu^{2+} ions. As has been reported before, Cu^{2+} , Fe^{3+} , and Mn^{3+} start to oxidize to Cu^{3+} , Fe^{4+} , and Mn^{4+} during charge at about 2.4, 3.8, and 3.6 V, respectively.^{18,33} Additionally, we confirmed the oxidation and reduction state of each transition-metal ion with the differential capacity



Figure 2. SEM and EDX mapping images of each ion in the (a) x = 0 and (b) x = 0.2 samples.

profiles of the first cycle (Figure S5). This means copper has an oxidation state of 2+ at the pristine state and that gets oxidized to 3+ first during charge compared with the other transition-metal ions. To verify this assertion, XPS analysis was carried out and the results are shown in Figure 3b. As seen in Figure 3b, the original oxidation state of each transition-metal ion in the x = 0.2 sample is 2+ for Cu, 3+ for Fe, and 3+/4+ for Mn, which are well matched with the compositional calculation of Cu^{2+} , Fe^{3+} , and $Mn^{3.x+}$ in the samples. The binding energy of each transition-metal ion is shifted to higher values when the cell is charged, indicating that all the three transition-metal ions are electrochemically active during cycling. Among them, the Cu²⁺ ions start to oxidize to 3+ first from 2.4 V compared to the Fe³⁺ and Mn³⁺ ions, which is consistent with the previous literature. Fe-ion migration is a critical problem for O3-type Fe-containing materials, so the decreased amount of Fe with the Cu substitution also helps increase the specific capacity. From these data, we confirm our assertion that the copper ions contribute to the increased capacity with increasing Cu content in the samples.

As already reported in the literature, iron migration during cycling is a critical problem with Fe-containing cathode materials for sodiumion batteries.^{4,8,18} Therefore, we recorded the ex-situ XRD patterns of both the x = 0 and 0.2 samples during the first cycle to explain the improvement in the discharge capacity from a structural stability perspective. Figure 3c and Figure S1 (see supplementary material) show the ex-situ XRD results of Na(Fe_{1/3}Mn_{2/3})O₂, Na[Cu_{0.1}(Fe_{1/3}Mn_{2/3})O₂, and Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})O₈]O₂ electrodes at different states of charge

(SOC) and depths of discharge (DOD). In the case of O3-type cathode materials, the intensity of the main peak at around $2\Theta = 41^{\circ}$ generally decreases and the peaks detected at $2\Theta = 30 - 35$ shift to lower angles and the peaks at $2\Theta = 35 - 40$ shift to higher angles during charge, indicating that the crystal structure changes from the O3-type rhombohedral structure to the P3-type monoclinic structure.¹⁸ As we anticipated, the Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ electrode with 20 atom% Cu shows less structural change than the Na[Cu_{0.1}(Fe_{1/3}Mn_{2/3})_{0.9}]O₂ and Na(Fe_{1/3}Mn_{2/3})O₂ electrodes during cycling. The Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ electrode slightly transformed to P3-type phase when the cell was charged to 4.3 V and then returned to the original O3-type structure when the cell was discharged. On the other hand, the Na(Fe_{1/3}Mn_{2/3})O₂ electrode shows a rapid phase change from the O3-type rhombohedral to the P3monoclinic structure during charge and the peaks become broadened when the cell was discharged. From these crystal structural change results, we confirm that the Cu substitution enhances the structural stability by suppressing the iron migration, which leads to an increase in specific capacity.

We also evaluated the cycle performances and rate capabilities of the samples to assess the benefits of Cu substitution (Figures 4a and 4b). For the cycle performance tests, all cells were tested with a constant current of 0.2C rate at room temperature. For the rate capability tests, all cells were charged to 4.3 V with a constant current of 0.1C rate and then discharged to 1.2 V with various currents from 0.1C rate to 2C rate. From these results, we could find that the



Figure 3. (a) Comparison of the first charge-discharge curves of Na/Na[$Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}$]O₂ cells (x = 0, 0.1, and 0.2). (b) XPS results of the x = 0.2 sample with different states of charge (SOC) in the first cycle (Black: pristine state, Red: middle of charge, Blue: end of charge in Fig. 3(a)). (c) Comparison of the structural change of the x = 0 and 0.2 samples with different SOC and depths of discharge (DOD) in the first cycle.

 $Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O_2$ electrode exhibits the best cycle retention of 70% during 30 cycles and good rate capability (124 mAh g⁻¹ at 0.2C rate and 70 mAh g⁻¹ at 2C rate) compared to the other samples. The Na(Fe_{1/3}Mn_{2/3})O₂ sample shows disappointing results in both cycle and rate performances.

We believe that these improved performances originate from the structural stability and suppression of Fe migration facilitated by Cu doping. We also confirmed the structural stability of the Cu-doped samples by ex-situ XRD after 30 cycles. As shown in Figure 4c, the crystal structure of the Na(Fe_{1/3}Mn_{2/3})O₂ electrode partially changed to P3-type monoclinic phase but the Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})O₂ electrode shows a single O3-type rhombohedral phase after 30 cycles. For further investigation of crystal structural changes after 30 cycles, we recorded the ex-situ HR-TEM and the corresponding electron diffrac-





Figure 4. (a) Cycling performance and (b) rate capability of the Na/Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]O₂ cells (x = 0, 0.1 and 0.2) charged with a current density of 12 mA g⁻¹ (0.1C rate) and discharged with different current densities (0.1C rate for cycle test, 0.1C to 2C rates for rate test) at 25°C. (c) Comparison of the ex-situ XRD results of the x = 0 and 0.2 electrodes after 30 cycles.

Downloaded on 2017-01-06 to IP 80.82.78.170 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Figure 5. HR-TEM bright field images and the corresponding electron diffraction patterns from each particle.

tion patterns (Figure 5). The Na(Fe_{1/3}Mn_{2/3})O₂ particle shows the P3-type monoclinic phase with the space group of C2/m after 30 cycles, while the Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ sample still preserves the original O3-type rhombohedral phase. Through these electrochemical performances and characterization data, we conclude that the Cu doping provides good structural stability and thereby leads to improved electrochemical performance.

As already shown by several groups, Na metal involves an unstable SEI layer and can be easily oxidized than Li metal during cycling, which can affect the electrochemical performances of the cathode materials.^{36,37} To measure the exact electrochemical characteristics of Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂, therefore, we assembled a full cell with the P-TiP₂-C alloy-type anode material that was developed by our group.³⁴ This material has nano-size particles and the SEM and XRD data of the samples are shown in Figure S2 (see supplementary material). This anode shows a high specific capacity of 733 mAh g^{-1} at 0.1C rate with excellent cycle retention at 0.2C rate during 100 cycles (see Figure S3). As shown in Figure 6a, we designed the ratio between the negative and positive electrode capacities (N/P ratio) as 1.3: 1 and the cutoff voltage as 1.2 - 4.2 V for the full cell. This full cell shows a reasonable specific capacity of 130 mAh g⁻¹ at 0.1C rate and 118 mAh g^{-1} at 0.2C rate in the first cycle at room temperature (Figure 6b). The remarkable point is good capacity retention during 100 cycles which is much better than half-cell results. Through the full cell test, therefore, we could confirm the real electrochemical performances of the cathode materials.

Conclusions

Although various types of cathodes and anodes are being intensively studied for sodium-ion cells, full cell data are rarely available in the literature. We presented here the performance of a full sodium-ion cell fabricated with a O3-type layered Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ cathode and an alloy-type P-TiP₂-C anode. To optimize and select the cathode composition for full cell, Na[Cu_x(Fe_{1/3}Mn_{2/3})_{1-x}]C₂O₄ samples with $0 \le x \le 0.2$ were synthesized and characterized. SEM EDX mapping confirmed that Cu is uniformly distributed in the sample. The x = 0.2 composition Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ showed a reasonable specific capacity, good cyclability, and high rate performance than the Na(Fe_{1/3}Mn_{2/3})O₂ sample with no Cu. Through ex-



Figure 6. (a) Comparison of the first charge-discharge curves of the cathode, anode, and full cell at 25°C. (b) Long-term cycle performances of the P-TiP₂-C / Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]O₂ full cell charged to 4.2 V and discharged to 1.2 V with a constant current of 12 mA g⁻¹ (0.1C rate) and 24 mA g⁻¹ (0.2C rate) at 25°C.

situ XRD and XPS studies, we confirmed the electrochemical activation and structural stabilization effect by Cu ions, which lead to good electrochemical performances. The enhanced performance of the Na[Cu_{0.2}(Fe_{1/3}Mn_{2/3})_{0.8}]C₂O₄ /P-TiP2-C full cell compared to that of the cathode with no Cu is due to the suppression of the phase transition during cycling from O3 to P3 structure imparted by Cu.

Acknowledgments

This work was supported by the Welch Foundation grant F-1254. The phosphorous-based anode work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DE-SC0005397.

References

- 1. B. Scrosati and J. Garche, *J. Power Sources*, **195**, 2419 (2010).
- 2. B. Dunn, H. Kamath, and J.-M. Tarascon, Science, 334, 928 (2011).
- S. Komaba, C. Takei, T. Nakayama, A. Ogata, and N. Yabuuchi, *Electrochem. Com*mun., 12, 355 (2010).
- 4. N. Yabuuchi, H. Yoshida, and S. Komaba, *Electrochemistry*, **80**, 716 (2012).
- 5. Y. Takeda, K. Nakahara, M. Nishijima, N. Imanishi, and O. Yamamoto, Mater. Re-
- search Bull., 29, 659 (1994).
 S. Okada, Y. Takahashi, T. Kiyabu, T. Doi, J. Yamaki, and T. Nishida, Proceedings of the 210th Meeting of the Electrochem. Soc., Cancun, Mexico (2006).
- 7. S. Komaba, N. Yabuuchi, T. Nakayama, A. Ogata, T. Ishikawa, and I. Nakai, *Inorg. Chem.*, **51**, 6211 (2012).
- N. Yabuuchi, M. Yano, H. Yoshida, S. Kuze, and S. Komaba, *J. Electrochem. Soc.*, 160, A3137 (2013).
- C. Didier, M. Guignard, C. Denage, O. Szajwaj, S. Ito, I. Saadoune, J. Darriet, and C. Delmas, *Electrochem. Solid-State Lett.*, 14, A75 (2011).
- D. Kim, E. Lee, M. Slater, W. Lu, S. Rood, and C. S. Johnson, *Electrochem. Commun.*, 18, 66 (2012).

- S.-M. Oh, S.-T. Myung, C. S. Yoon, J. Lu, J. Hassoun, B. Scrosati, K. Amine, and Y.-K. Sun, *Nano Lett.*, 14, 1620 (2014).
- M. Sathiya, K. Hemalatha, K. Ramesha, J.-M. Tarascon, and A. S. Prakash, *Chem. Mater.*, 24, 1846 (2012).
- S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takei, S. Takada, A. Hokura, and I. Nakai, *ECS Trans.*, 16, 43 (2009).
- S.-M. Oh, S.-T. Myung, M.-W. Jang, B. Scrosati, J. Hassoun, and Y.-K. Sun, *Phys. Chem. Chem. Phys.*, **15**, 3827 (2013).
- B. Mortemard de Boisse, D. Carlier, M. Guignard, and C. Delmas, J. Electrochem. Soc., 160, A569 (2013).
- 16. X. Xia and J. R. Dahn, *Electrochem. Solid-State Lett.*, 15, A1 (2012).
- 17. H. Yoshida, N. Yabuuchi, and S. Komaba, *Electrochem. Commun.*, **34**, 60 (2013).
- S.-M. Oh, S.-T. Myung, J.-Y. Hwang, B. Scrosati, K. Amime, and Y.-K. Sun, *Chem. Mater.*, 26, 6165 (2014).
- J.-Y. Hwang, S.-M. Oh, S.-T. Myung, K. Y. Chung, I. Belharouak, and Y.-K. Sun, *Nat. Commun.*, 6, 6865 (2015).
- L. Mu, S. Xu, Y. Li, Y.-S. Hu, H. Li, L. Chen, and X. Huang, *Adv. Mater.*, 27, 6928 (2015).
- N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, and S. Komaba, *Nat. Mater.*, 11, 512 (2012).
- 22. R. Berthelot, D. Carlier, and C. Delmas, Nat. Mater., 10, 74 (2011).
- 23. Z. Lu and J. R. Dahn, J. Electrochem. Soc., 148, A1225 (2001).
- D. Buchholz, L. G. Chagas, M. Winter, and S. Passerini, *Electrochim. Acta*, 110, 208 (2013).

- 25. A. Bhide and K. Hariharan, Solid State Ionics, 192, 360 (2011).
- 26. D. Yuan, X. Hu, J. Qian, F. Pei, F. Wu, R. Mao, X. Ai, H. Yang, and Y. Cao, *Electrochim. Acta*, **116**, 300 (2014).
- D. Yuan, W. He, F. Pei, F. Wu, Y. Wu, J. Qian, Y. Cao, X. Ai, and H. Yang, J. Mater. Chem. A, 1, 3895 (2013).
- M. D'Arienzo, R. Ruffo, R. Scotti, F. Morazzoni, C. M. Mari, and S. Polizzi, *Phys. Chem. Chem. Phys.*, 14, 5945 (2012).
- Y. Li, Z. Yang, S. Xu, L. Mu, L. Gu, Y.-S. Hu, H. Li, and L. Chen, *Adv. Sci.*, 2, 1500031 (2015).
- M. Nose, H. Nakayama, K. Nobuhara, H. Yamaguchi, S. Nakanishi, and H. Iba, J. Power Sources, 234, 175 (2013).
- P. Barpanda, J. Lu, T. Ye, M. Kajiyama, S.-C. Chung, N. Yabuuchi, S. Komaba, and A. Yamada, *RSC Adv.*, 3, 3857 (2013).
- P. Barpanda, T. Ye, M. Avdeev, S.-C. Chung, and A. Yamada, J. Mater. Chem. A, 1, 4194 (2013).
- Y. Ono, Y. Yui, M. Hayashi, K. Asakura, H. Kitabayashi, and K. I. Takahashi, ECS Trans., 58, 33 (2014).
- 34. S.-O. Kim and A. Manthiram, Chem. Mater., 28, 5935 (2016).
- X. Wang, G. Liu, T. Iwao, M. Okubo, and A. Yamada, J. Phys. Chem. C, 118, 2970 (2014).
- A. Rudola, D. Aurbach, and P. Balaya, *Electrochem. Commun.*, 46, 56 (2014).
- D. I. Iermakova, R. Dugas, M. R. Palacin, and A. Ponrouch, *J. Electrochem. Soc.*, 162, A7060 (2015).