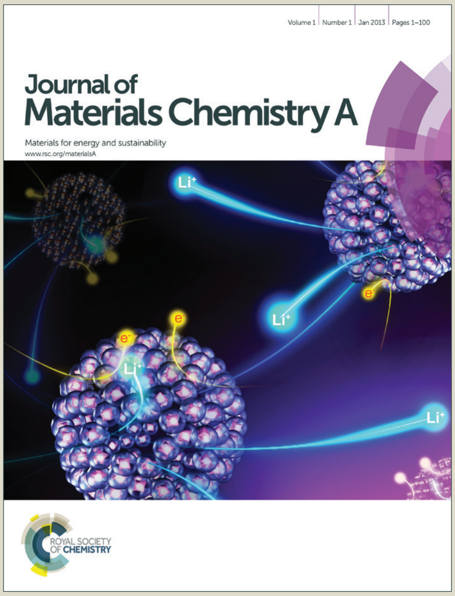
Journal of Materials Chemistry A

Accepted Manuscript



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

Journal of Materials Chemistry A

Materials for energy and sustainability

www.rsc.org/materialsA

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

Journal Name RSCPublishing

COMMUNICATION

Alluaudite $LiMnPO_4$: New Mn-based positive electrode for Li rechargeable battery

Cite this: DOI: 10.1039/x0xx00000x

Jongsoon Kim,[a] Hyungsub Kim,[a] Kyu-Young Park,[a] Young-Uk Park,[a] Seongsu Lee,[b] Hyung-Soon Kwon, [a] Han-Ill Yoo, [a] and Kisuk Kang [a*]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A novel, Na-pillared $LiMnPO_4$ ($Li_{0.78}Na_{0.22}MnPO_4$) with an alluaudite structure is successfully prepared for the first time and proposed as a new positive electrode for Li rechargeable batteries. Approximately 0.8 Li^+ are reversibly extracted from and reinserted into $LiMnPO_4$ via Mn^{2+}/Mn^{3+} redox reactions. The alluaudite $LiMnPO_4$ (*a*-$LiMnPO_4$) structure is sufficiently robust during repeated Li extraction/insertion such that ~92% of the initial capacity is retained after 50 charge/discharge cycles. An *ex-situ* XRD study of the electrochemical cell during cycling indicates that Li de/intercalation in alluaudite $LiMnPO_4$ occurs via the one-phase (solid-solution) reaction instead of the two-phase reaction observed in olivine $LiMnPO_4$.

Environmental concerns about air pollution and the greenhouse effect have resulted in an intense search for novel, eco-friendly vehicles equipped with emission-less power systems.[1-4] Because of their high energy and power density, Li rechargeable batteries are promising candidates for use in these power systems.[5-7] Positive electrodes based on an olivine structure have attracted attention for use in Li ion batteries. The strong covalent P-O bond in the olivine structure leads to high safety and stability in battery applications, and high power capability has recently demonstrated in olivine positive electrodes.[7-10] Over the past decade, various promising olivine positive electrode materials, including $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, and $Li(Fe_xMn_yCo_z)PO_4$, have been identified and physico-chemically characterized.[11-15]

Herein, we report novel Li-Mn-P-O chemistry in an alluaudite crystal structure. While the alluaudite material, alluaudite $LiMnPO_4$ (*a*-$LiMnPO_4$), has a chemical composition similar to that of olivine $LiMnPO_4$, its electrochemical properties, including the voltage and its phase reaction with Li, are fundamentally different. Moreover, *a*-$LiMnPO_4$ positive electrode exhibited highly reversible Li insertion and extraction posing it as a promising positive electrode candidate for Li rechargeable batteries. It is expected that $LiMnPO_4$ with alluaudite crystal structure can also serve as a comparative platform for gaining new insight into olivine $LiMnPO_4$.

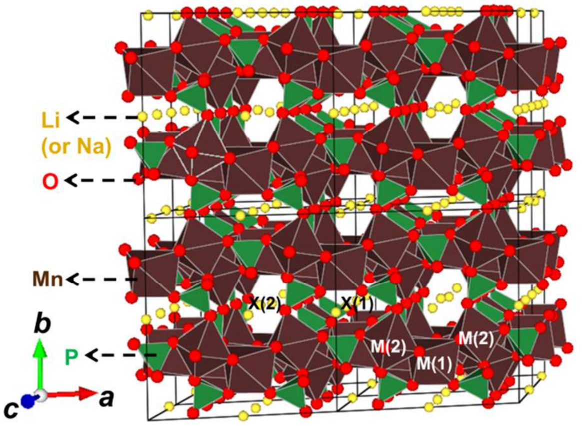
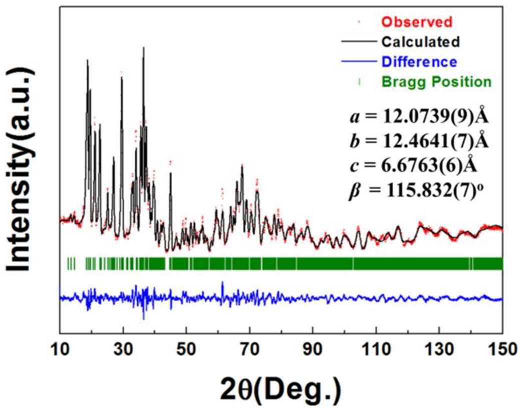


Figure 1 The schematic representation of the alluaudite $A_{0.67}MnPO_4$ (A = Na or Li).

As determined by Moore in 1971, the general crystal structural formula of alluaudite is $X(2)X(1)M(1)(M(2))_2(PO_4)_3$ with a monoclinic C2/*c* space group.[16-20] As illustrated in Figure 1, the open structure includes a succession of two hexagonal tiers, X(1) or X(2), that form plausible one-dimensional (1-D) diffusion channels along the *c*-axis. The $M(2)O_6$ octahedra are linked by highly-distorted $M(1)O_6$ octahedra with edge-sharing in the *ac* plane. Mn can occupy M(1) and M(2) sites. X(1) and X(2) are filled with monovalent cations, such as Na or Li.

To prepare *a*-$LiMnPO_4$, a novel Mn-based alluaudite $Na_2Mn_3(PO_4)_3$ (= $Na_{0.67}MnPO_4$) was synthesized as a precursor for $Li_{0.67}MnPO_4$. Subsequently, *a*-$LiMnPO_4$ was prepared by (1) ion-exchange from $Na_{0.67}MnPO_4$ to $Li_{0.67}MnPO_4$ and (2) an additional lithiation process. As reported in previous studies, the alluaudite structure has additional sites in which monovalent cations can be intercalated.[17, 18, 21] The presence of Mn^{3+} in the alluaudite structure was expected to enable intercalation of additional Li^+ or Na^+ ions.



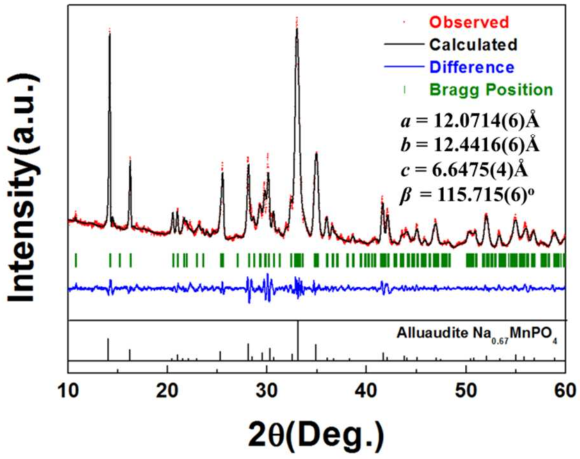
Atom	Multiplicity	x	y	z	B_{iso}	Occupancy
Na1	4	0	0.5	0	1.7(13)	1
Na2	4	0	-0.0311(16)	0.25	1.3(16)	1
Mn1	4	0	0.2762(14)	0.25	1.59(17)	1
Mn2	8	0.2810(7)	0.6541(7)	0.3659(13)	1.32(3)	1
P1	4	0	0.7181(9)	0.25	1.45(8)	1
P2	8	0.2353(8)	0.8865(7)	0.1292(14)	2.13(11)	1
O1	8	0.4574(8)	0.7142(7)	0.5403(13)	2.03(12)	1
O2	8	0.1015(7)	0.6392(7)	0.2483(12)	2.13(13)	1
O3	8	0.3390(7)	0.6602(6)	0.1001(12)	2.38(11)	1
O4	8	0.1331(7)	0.3949(7)	0.3209(13)	2.21(12)	1
O5	8	0.2276(7)	0.8193(6)	0.3135(13)	2.11(15)	1
O6	8	0.3236(7)	0.5076(6)	0.3833(13)	2.32(11)	1

R_P = 3.69%, R_I = 5.99%, R_F = 4.06%, χ^2 = 6.14%

Figure 2 The refined ND pattern and atomic position and occupancy of alluaudite $Na_{0.67}MnPO_4$ (R_P = 3.69%, R_I = 5.99%, R_F = 4.06%, χ^2 = 6.14%)

A previous investigation of alluaudite materials reported failure of the synthesis of $Na_{0.67}MnPO_4$.[19] In this study, which was consistent with the previous report, the phase of the $Na_{0.67}MnPO_4$ synthesized under atmospheric conditions was not alluaudite; instead, the phase of the resulting material was fillowite, containing Mn only in the +2 valence state.[19, 22] Varying the synthesis temperature did not yield the alluaudite phase (Supporting Figure. S1). However, under controlled oxidizing environments, phase-pure alluaudite $Na_{0.67}MnPO_4$ was obtained, thereby suggesting that a critical factor for synthesis of alluaudite $Na_{0.67}MnPO_4$ is the maintenance of oxidizing conditions during calcination to stabilize mixed Mn valency (Mn^{2+} and Mn^{3+}). Structural analyses by the neutron diffraction (ND, Figure 2) and X-ray diffraction (XRD, Supporting Figure S2) indicated that the alluaudite $Na_{0.67}MnPO_4$ was isostructural with other known alluaudite compounds, such as $Na_2Fe_3(PO_4)_3$[23] and $Na_2FeMn_2(PO_4)_3$[19] with a monoclinic space group. No impurities or contamination were detected. The Rietveld refinement of the ND pattern (lattice parameters of a = 12.0739(9)Å, b = 12.4641(7)Å, c = 6.6763(6)Å, and β = 115.832(7)°) was consistent with the results from XRD refinement (Supporting Table S1). The fit was satisfactory, with low R-factors, thereby indicating the proper structural model. The detailed crystal structure of $Na_{0.67}MnPO_4$ obtained by ND analysis is tabulated in Figure 2.

Alluaudite $Li_{0.67}MnPO_4$, which is the partially delithiated phase of a-$LiMnPO_4$, was synthesized from well-crystallized alluaudite $Na_{0.67}MnPO_4$. Alluaudite $Li_{0.67}MnPO_4$ was prepared using the soft chemical ion-exchange method. The reaction time was critical for exchange between Na and Li, as well as for the stability of the alluaudite crystal structure. The exchange of Na for Li was promoted by long ion-exchange reaction times; however, alluaudite $Na_{0.67}MnPO_4$ was partially converted into olivine $LiMnPO_4$ at longer reaction time (Supporting Figure S3). Thus, the optimum reaction time was a compromise between maximum ion exchange and maintenance of the pure alluaudite $Li_{0.67}MnPO_4$ structure. All Na ions could not be exchanged for Li ions in the alluaudite structure, and some residual Na ions must be present in the alluaudite structure for stabilization. The chemical composition of the ion-exchanged Li phase was $Li_{0.47}Na_{0.2}MnPO_4$ (=a-$Li_{0.67}MnPO_4$) based on inductively coupled plasma (ICP) measurements.



Atom	Multiplicity	x	y	z	B_{iso}	Occupancy
Li1	4	0	0.5	0	2.5(17)	0.44(2)
Na1	4	0	0.5	0	2.9(15)	0.404 (12)
Li2	4	0	0.039(6)	0.25	2.1(11)	0.64(2)
Na2	4	0	0.039(6)	0.25	2.4(13)	0.323 (13)
Mn1	4	0	0.265(2)	0.25	1.36(11)	1
Mn2	8	0.2721(13)	0.6574(12)	0.358(3)	1.54(13)	1
P1	4	0	0.7190(17)	0.25	1.26(15)	1
P2	8	0.2363(12)	0.8893(10)	0.123(2)	1.36(12)	1
O1	8	0.4581(12)	0.7189(9)	0.552(2)	1.94(12)	1
O2	8	0.0934(11)	0.6382(9)	0.2290(20)	1.35(11)	1
O3	8	0.3409(10)	0.6658(8)	0.1070(17)	1.12(13)	1
O4	8	0.1261(11)	0.3954(10)	0.331(2)	1.62(13)	1
O5	8	0.2258(11)	0.8258(11)	0.320(2)	1.57(12)	1
O6	8	0.3176(11)	0.4940(10)	0.366(2)	1.73(11)	1

R_P = 6.41%, R_I = 1.94%, R_F = 1.58%, χ^2 = 8.26%

Figure 3 The refined XRD pattern and atomic position and occupancy (ND pattern) of alluaudite $Li_{0.67}MnPO_4$ (R_P = 6.41%, R_I = 1.94%, R_F = 1.58%, χ^2 = 8.26%).

Figure 3 shows the XRD pattern of a-$Li_{0.67}MnPO_4$. The general pattern was similar to that of $Na_{0.67}MnPO_4$, indicating that the overall crystal structure was maintained. No contamination or secondary phases were detected. The lattice parameters of a-$Li_{0.67}MnPO_4$ (a = 12.0714(6)Å, b = 12.4416(6)Å, c = 6.6475(4)Å, and β = 115.715(6)°) were smaller than those of $Na_{0.67}MnPO_4$ due to the smaller ionic radius of the Li^+ ion (r = 0.74Å) compared with that of the Na^+ ion (r = 1.02Å). To clearly determine the crystal structure of a-$Li_{0.67}MnPO_4$, ND analysis was performed (Supporting Figure S4). The detailed refinement of the atomic position and site occupancy of each atom is provided at the bottom of Figure 3. No major structural deviations were observed after the ion-exchange process. In Supporting Figure S5 and S6, EIS experiments revealed that this material has relatively high electrical conductivity of ~1.65×10^{-8} S cm^{-1} at room temperature, which is comparable to that of olivine $LiFePO_4$ and is far higher than that of olivine $LiMnPO_4$.[24] The measured activation energy (Ea) of ~320 meV is also lower than those of other polyanion-based cathodes for Li rechargeable batteries such as $LiFePO_4$ (~600 meV), implying that reasonably high rate capability can be expected for the alluaudite $LiMnPO_4$.

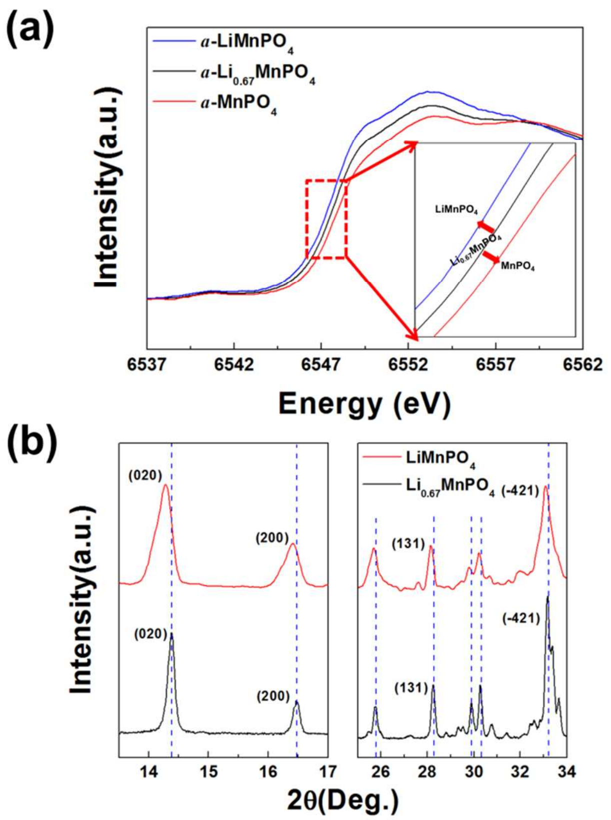


Figure 4 (a) Normalized Mn K-edge XANES spectra for alluaudite Li_xMnPO_4, (b) Comparison of XRD patterns between alluaudite $Li_{0.67}MnPO_4$ and alluaudite $LiMnPO_4$

The *a*-$LiMnPO_4$ was obtained after the additional lithiation of *a*-$Li_{0.67}MnPO_4$. The lithiation process was accompanied by continuous lattice changes and the reduction of Mn valency in the phase, as shown in Figure 4. X-ray absorption spectroscopy (XAS) in Figure 4(a) was used to compare the Mn K-edge X-ray absorption near-edge structure (XANES) spectra of the *a*-$MnPO_4$, *a*-$Li_{0.67}MnPO_4$, and *a*-$LiMnPO_4$. When additional Li ions were intercalated into the structure, the Mn K-edge of pristine *a*-$Li_{0.67}MnPO_4$ shifted toward the lower energy state. This result indicates that Mn^{3+} ions in *a*-$Li_{0.67}MnPO_4$ were reduced to a lower valence state (Mn^{2+}). For comparison, full delithiation of *a*-$Li_{0.67}MnPO_4$ resulted in the shift of the Mn K-edge towards a high-energy state, which was indicative of the reversible transition between Mn^{2+} and Mn^{3+}. As indicated in Figure 4(b), the lithiation of *a*-$Li_{0.67}MnPO_4$ led to continuous shifts of the XRD peaks, including (020), (200), (-421) and (-132) without evolution of new peaks.

Electrochemical measurements were performed with a Li metal anode in a 2016-type coin cell at 298 K. The charge/discharge was highly reversible for repeated cycles. As indicated in Figure 5(a) and 5(b), at a C/5 current rate, the discharge capacity was ~120 mAh g^{-1}, which corresponds to reversible intercalation of 0.7 Li^+ ions. The invariance of the charge/discharge profile over many cycles indicates that the structural integrity of the alluaudite framework was maintained during cycling. Based on the results, we speculated that 0.2 Na^+ ions were immobile (not exchanged for Li^+ ions) during electrochemical cycling and retained the overall structure during the ion-exchange process.

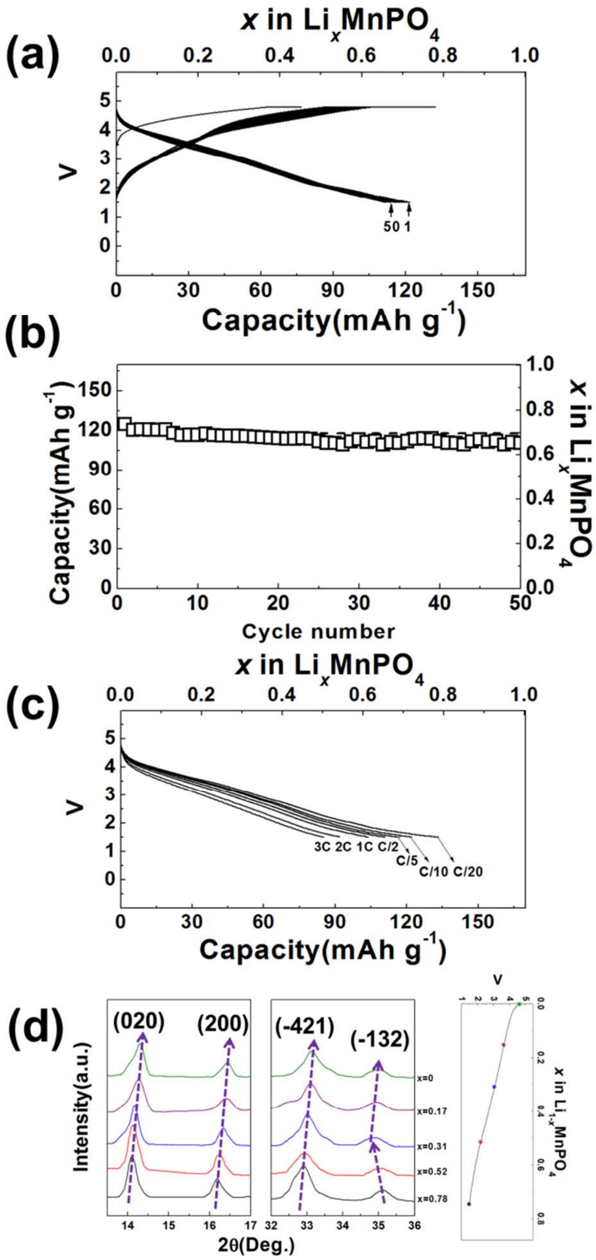


Figure 5 (a) Galvanostatic curves of alluaudite $LiMnPO_4$ during 50 cycles at C/5, (b) Cyclability of alluaudite $LiMnPO_4$ during 50 cycles at C/5, (c) Discharge curves of alluaudite $LiMnPO_4$ as a function of C rate from C/20 to 3C (Charging at CCCV mode (C/20 rate and 5 hour holding at 4.8V)), (d) *Ex-situ* XRD patterns of *a*-Li_xMnPO_4 ($0 \le x \le 0.8$) with the discharge profile.

The stable electrochemical reaction enabled ~92% capacity retention after 50 cycles, as shown in Figure 5(b). Figure 5(c) shows that ~0.8 Li^+ ions could be reversibly extracted and reinserted into the structure (= ~140 mA h g^{-1}) at a slower rate. On the other hand, under battery operation at higher current densities (Figure 5(c)), ~78% of the initial capacity could be delivered in 1 hour (1C rate), and ~64% could be delivered in 20 min (3C rate). These results suggested that the alluaudite electrode could sustain a respectable rate capability not achievable with olivine $LiMnPO_4$.[25, 26] In *ex-situ* XRD measurements along discharge in Figure 5(d), the main alluaudite peaks gradually shifted as a function of Li content, thus indicating the one-phase reaction. One-phase reaction is also observed in alluaudite $LiFePO_4$ positive electrode, which suggests that one-phase electrochemical reaction is generally characteristic of alluaudite electrode materials. This is a clear contrast to olivine $LiMnPO_4$, which is known to exhibit two-phase reaction during de/lithiation.

It is noteworthy that the average redox potential of *a*-$LiMnPO_4$ (~3.5V *vs.* Li^+) was lower than that of olivine $LiMnPO_4$ (~4.1V *vs.* Li^+). The discrepancy in the average redox potential can be attributed to the distinct local environments surrounding the redox element (Mn) in each structure. In the alluaudite framework, an MnO_6 octahedra shares the edge with other MnO_6; in contrast, the olivine framework has corner-sharing MnO_6 octahedra. This difference results in larger overlap of Mn orbital in alluaudite than that in olivine structure.[27] The more extensive orbital overlap in the alluaudite structure raises the energy level of the electron, thus lowering the energy cost of extracting electrons from the Mn (*i.e.* redox potential). The redox potential is also influenced by the inductive effect associated with P-O bonding in alluaudite and olivine. While there are edge-sharing PO_4 tetrahedral around MnO_6 in the olivine structure, only corner-sharing PO_4 groups exist in the alluaudite structure.[28] This structural difference results in weaker inductive effect in alluaudite than that in olivine, thereby leading to lower redox potential.

In summary, non-olivine $LiMnPO_4$ with an alluaudite structure was successfully prepared from newly synthesized alluaudite $Na_{0.67}MnPO_4$ using an ion-exchange process. Approximately 0.8 Li^+ ions in *a*-$LiMnPO_4$ could be reversibly intercalated and deintercalated at reasonably fast rates over long cycles, thereby indicating that *a*-$LiMnPO_4$ is a promising positive electrode material for Li ion batteries. Comparative studies with compositionally similar olivine $LiMnPO_4$ indicated that the electrochemical mechanism and redox potential of *a*-$LiMnPO_4$ are fundamentally different from those of olivine $LiMnPO_4$. The development of a novel *a*-$LiMnPO_4$ not only provides a promising new Mn-based positive electrode, but also broadens the scope of our understanding of Li-Mn-P-O chemistry.

This work was supported by Energy Efficiency and Resources R&D program (20112020100070) under the Ministry of Knowledge Economy, Republic of Korea, and by Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (20114010203120).

Notes and references

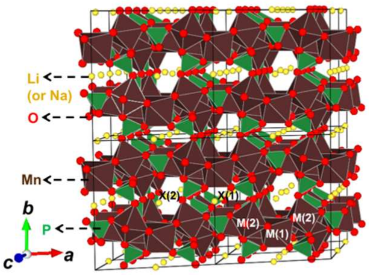
[a] Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-742, Korea.

[b] Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong-gu, Daejeon 305-600, Korea.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1. P. S. Herle, B. Ellis, N. Coombs and L. F. Nazar, *Nat. Mater.*, 2004, **3**, 147-152.
2. S. Nishimura, G. Kobayashi, K. Ohoyama, R. Kanno, M. Yashima and A. Yamada, *Nat. Mater.*, 2008, **7**, 707-711.
3. X. G. Zhang, X. D. Zhang, W. He, Y. Z. Yue, H. Liu and J. Y. Ma, *Chem. Commun.*, 2012, **48**, 10093-10095.
4. X. M. Liu, P. Yan, Y. Y. Xie, H. Yang, X. D. Shen and Z. F. Ma, *Chem. Commun.*, 2013, **49**, 5396-5398.
5. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.
6. B. Kang and G. Ceder, *Nature*, 2009, **458**, 190-193.
7. Y. S. Hu, Y. G. Guo, R. Dominko, M. Gaberscek, J. Jamnik and J. Maier, *Adv. Mater.*, 2007, **19**, 1963-+.
8. Y. G. Wang, P. He and H. S. Zhou, *Energy Environ. Sci.*, 2011, **4**, 805-817.
9. J. Kim, K. Y. Park, I. Park, J. K. Yoo, J. Hong and K. Kang, *J. Mater. Chem.*, 2012, **22**, 11964-11970.
10. S. Y. Chung, J. T. Bloking and Y. M. Chiang, *Nat. Mater.*, 2002, **1**, 123-128.
11. K. Y. Park, J. Hong, J. Kim, Y. U. Park, H. Kim, D. H. Seo, S. W. Kim, J. W. Choi and K. Kang, *J. Electrochem. Soc.*, 2013, **160**, A444-A448.
12. J. Kim, Y. U. Park, D. H. Seo, J. Kim, S. W. Kim and K. Kang, *J. Electrochem. Soc.*, 2011, **158**, A250-A254.
13. S. K. Martha, B. Markovsky, J. Grinblat, Y. Gofer, O. Haik, E. Zinigrad, D. Aurbach, T. Drezen, D. Wang, G. Deghenghi and I. Exnar, *J. Electrochem. Soc.*, 2009, **156**, A541-A552.
14. A. Yamada, Y. Kudo and K. Y. Liu, *J. Electrochem. Soc.*, 2001, **148**, A1153-A1158.
15. G. Kobayashi, A. Yamada, S. Nishimura, R. Kanno, Y. Kobayashi, S. Seki, Y. Ohno and H. Miyashiro, *J. Power Sources*, 2009, **189**, 397-401.
16. P. B. Moore, *Am. Miner.*, 1971, **56**, 1955.
17. K. Trad, D. Carlier, L. Croguennec, A. Wattiaux, M. Ben Amara and C. Delmas, *Inorg. Chem.*, 2010, **49**, 10378-10389.
18. K. Trad, D. Carlier, L. Croguennec, A. Wattiaux, M. Ben Amara and C. Delmas, *Chem. Mater.*, 2010, **22**, 5554-5562.
19. T. J. Richardson, *J. Power Sources*, 2003, **119**, 262-265.
20. J. Kim, H. Kim, I. Park, Y. U. Park, J. K. Yoo, K. Y. Park, S. Lee and K. Kang, *Energy Environ. Sci.*, 2013, **6**, 830-834.
21. F. Hatert, P. Keller, F. Lissner, D. Antenucci and A. M. Fransolet, *Euro. J. Miner.*, 2000, **12**, 847-857.
22. D. Antenucci, P. Tarte and A. M. Fransolet, *N. J. F. Miner.*, 1996, 289-296.
23. F. Hatert, L. Rebbouh, R. P. Hermann, A. M. Fransolet, G. J. Long and F. Grandjean, *Am. Miner.*, 2005, **90**, 653-662.
24. C. Delacourt, L. Laffont, R. Bouchet, C. Wurm, J. B. Leriche, M. Morcrette, J. M. Tarascon and C. Masquelier, *J. Electrochem. Soc.*, 2005, **152**, A913-A921.
25. G. H. Li, H. Azuma and M. Tohda, *Electrochem. Solid State Lett.*, 2002, **5**, A135-A137.
26. A. Yamada, M. Hosoya, S.-C. Chung, Y. Kudo, K. Hinokuma, K.-Y. Liu and Y. Nishi, *J. Power Sources*, 2003, **119-121**, 232-238.
27. F. Zhou, C. A. Marianetti, M. Cococcioni, D. Morgan and G. Ceder, *Phy.Rev. B*, 2004, **69**, 4.
28. A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1609-1613.

Table of contents



A novel, Na-pillared $LiMnPO_4$ with an alluaudite structure is allows fast lithium diffusion with stable electrochemical cycling as a cathode in lithium batteries.