Nowadays rechargeable aluminum batteries are envisaged as a future alternative to lithium ion batteries. However, the development of electrodes and non-aqueous electrolyte solutions for aluminum batteries is still a great challenge. Layered-type molybdate (α-MoO₃) is studied here as a positive electrode for Al metal battery and ionic liquid is used as electrolyte solution. The observed maximum gravimetric capacity is 100 mAh g⁻¹, although only a few discharge-charge cycles were successfully carried out and the capacity falls quickly. According to electrochemical, XRD, NMR, microanalysis and XPS results, aluminum cation is intercalated in the interlayer space (van der Waals gap) between the octahedron layers (MoO₆) while the main framework is preserved. Because of the intercalation of aluminum and the reduction of molybdenum, the interlayer spacing of Al₅-MoO₃ is reversibly increased compared to pristine molybdate. The intercalation of aluminum into molybdate is a slow process and rather limited to the region near the surface of the particles. © The Author(s) 2018. 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: 10.1149/2.0391813jes]

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Irrespectively of their great commercial success, lithium batteries are not exempt from drawbacks, such as high cost, safety issues and low natural abundance of lithium in the earth crust. According to several authors, aluminum batteries may be an alternative to lithium ones, particularly in terms of cost, safety and volumetric capacity. However, the development of rechargeable aluminum batteries remains very challenging. A main drawback is the difficulty to find a positive electrode material being able to intercalate reversibly aluminum, in the form of cation (Al(III)) or anions (e.g. AlCl₄⁻). Another drawback is to find an electrolyte solution suitable for reversible plating/stripping of Al and also stable within the operation voltage of the working electrode. Although ionic liquids can allow plating/stripping of aluminum, electrode corrosion and side-reactions can take place in the aluminum batteries.¹¹

Using room temperature chloroaluminates ionic liquids as electrolytes for aluminum battery was early reported in the 1980’s decade.¹²,¹³ Mohandas et al. found that, in sodium chloroaluminate melt saturated with sodium chloride at 175°C, the anodic process observed on graphite electrode is due to the oxidative intercalation of chloroaluminate into graphite, and they concluded that the anion intercalation reactions occur only if the charge voltage is higher than the chlorine evolution potential (2Cl⁻ → Cl₂ + 2e⁻ at 2.2 V vs. Al). High-performance batteries based on the intercalation of AlCl₄⁻ into graphite at room temperature were recently reported.¹⁴ Besides chloroaluminate intercalation, several groups have claimed intercalation of aluminum cation into transition metal oxides, such as V₂O₅,¹⁶ VO₂,¹⁷ TiO₂,¹⁸ and also into Mo₅S₈ Chevrel phases.¹⁹ The small size of aluminum ion could induce little change of the lattice parameters and this fact would be beneficial for electrochemical cycling. However, compared to lithium, there are only a few materials reported to be suitable for reversible intercalation of aluminum. A drawback is that the high charge density of Al(III) leads to strong interactions with the host framework and the diffusion rate usually is slow. Layered transition metal oxides can be important electrode materials for batteries based on multivalent ions.²⁰ There are reports about intercalation of aluminum into layered MoO₃ using an aqueous solution showing that the nature of MoO₃ is not strongly altered upon electrochemical intercalation of aluminum.²¹,²² Although Wang et al. used aqueous electrolytes in their electrochemical cells for Al-ion capacitors,²³ their theoretical calculations found that the intercalation of Al³⁺ into MoO₃ can take place even more easily than lithium and magnesium.

In this work, we study the electrochemical reaction between aluminum intercalation and MoO₃, for a rechargeable Al battery and using ionic liquid as electrolyte solution at room temperature. The electrochemical performance and the reaction mechanism are explored.

Materials and Methods

Raw MoO₃ (99.97% purity) sample and all other chemicals were purchased from Sigma Aldrich. The crystalline structures were studied by X-ray diffraction (XRD) using a Bruker D8 instrument with Cu Kα radiation. For the refinement of XRD patterns the software Topas was used. The XRD pattern of pristine MoO₃ was refined using the Rietveld method, while the LeBail method was preferred for discharged/charged electrodes.

The chemical compositions of the electrodes were analyzed by using X-ray microanalysis coupled to a FE-SEM JSM 7800F instrument with ED S detector. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a SPECs Phoibos 150 MCD instrument, equipped with Mg Kα source. The electrodes for ex-situ XPS and microanalysis studies were previously washed using dry methanol to remove traces of electrolyte and then dried at room temperature under inert atmosphere.

The ²⁷Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were obtained on a Bruker DRX-400 instrument operating at 104.2 MHz using a 5 mm broad band probe operating at 298 K. Typical acquisition conditions included between 16 and 64 scans averaging, 1 s recycle delay, 8 K complex points using a 600 ppm spectral width. Chemical shifts were referenced to a secondary standard 1 M Al[Cl(H₂O)₆]₃⁻ (isomer shift δ = 0.0 ppm).

The electrochemical experiments were carried out in a VMP-Biologic instrument, and using three-electrode cells (T-shape) with glassy carbon rods (Goodfellow) of 7.0 mm in diameter as current collectors. The Swagelok-type electrochemical cells were assembled in an M-Braun glove-box filled with Ar. High-purity (99.999%) Al discs were used as reference and counter electrodes. To prepare the working electrode, the active material (MoO₃, 80% wt) was mixed with binder (PFTFE, 10% wt) and carbon black (10% wt), and the mixture with n-methyl-2-pyrrolidone was pasted on a Pt disc. The Pt disc (Goodfellow, 99.95% purity) was 6.0 mm in diameter and 0.125 mm in thickness. The amount of molybdate deposited on the Pt disc was about 2.0 mg. In order to prevent corrosion because of using ionic liquid, iron, nickel and other metals currently used in batteries as current collectors were avoided. Two Whatman glass fiber filter papers soaked with five drops of the electrolyte solution were used as...
Figure 1. CV results of aluminum cells. (A) without active material and (B) with MoO$_3$ as working electrode at scan rate of 10 mV s$^{-1}$, and (C) with MoO$_3$ at 0.5 mV s$^{-1}$. (D) Peak intensity as a function of sweep rate.

Separators. The ionic liquid used as electrolyte solution was prepared in the dry box under Ar atmosphere by dissolving anhydrous AlCl$_3$ (99.999% purity) in 1-ethyl-3-methylimidazolium chloride (EMIC) in molar ratio AlCl$_3$:EMIC = 1.1:1.0 (slightly acidic melt).

Results and Discussion

Electrochemistry.—The ionic liquid electrolyte contains simple and complex ions as Al$^{3+}$, Cl$^-$, AlCl$_4^-$ and Al$_2$Cl$_7^-$ . The equilibrium between these ions facilitates the redox reactions in the electrodes. In the case of acidic melt, the main electroactive species for Al deposition is expected to be Al$_2$Cl$_7^-$ . In the cyclic voltammetry (CV) results of the blank experiment with no active material and plotting the current intensity normalized by the electrode area (Fig. 1A), it is observed that the electrolyte solution based on ionic liquid is electrochemically stable in the voltage range between 0.0 and 2.1 V vs. Al. Below 0.0 V plating of Al takes place onto the Pt electrode during the cathodic sweep, and the stripping is observed at ca. 0.1 V during the anodic sweep. Otherwise, the ionic liquid is oxidized to Cl$_2$ over ca. 2.2 V. In addition, activation reactions could happen in the electrolyte solution and in the Al electrode during the first few cycles, such as removal of the passivating layer on Al surface.

The electrochemical behavior of as-received molybdate sample, with particle size of around 2–5 μm, was studied in aluminum cell. In the voltage range within the redox stability window of the electrolyte solution, and below the chlorine evolution potential, MoO$_3$ certainly exhibits electrochemical activity (Fig. 1B). The lack of relatively intense and narrow peaks in the CV suggests that the aluminum intercalation process would be slow and that the redox process could happen only in the region near the surface of the particles, similarly to a pseudocapacitance. At lower scan rate and imposing a narrower voltage window (Fig. 1C), it is observed that the main reduction peak is placed at ca. 1.1 V, while most of the oxidation process occurs between 1.2 and 1.9 V, out of the Al plating and chlorine evolution voltages. From the CV results obtained at several rates, and plotting logarithm of the intensity peak against the logarithm of the sweep rate (Fig. 2D), it is observed that the main reduction peak is placed at ca. 1.1 V, while most of the oxidation process occurs between 1.2 and 1.9 V, out of the Al plating and chlorine evolution voltages. From the CV results obtained at several rates, and plotting logarithm of the intensity peak against the logarithm of the sweep rate, the resulting slope can be understood on the basis of diffusion and/or capacitive processes (Fig. 2D). The relationship between the peak current (i) and the scan rate (v) is given by the power law $i = av^b$. When the redox reaction is controlled by diffusion $b = 0.5$, while for a capacitive behavior $b = 1.0$. In the case of the reduction peak near 1 V, the resulting value $b = 0.59$ agrees well with a reaction of aluminum with molybdate controlled by diffusion.

On the other hand, it is worth to note that these electrochemical experiments, both CV (Fig. 1) and galvanostatic (Fig. 2) tests, were carried out starting by a reduction process in the working electrode (MoO$_3$) and, consequently, the first discharge reaction cannot be attributed to any reaction related to previous chlorine evolution and, thus, the discharge reaction should be rather attributed to cationic intercalation (near particle surface or in bulk of MoO$_3$) or, alternatively,
to a conversion reaction, but not to intercalation of anion. In the literature, there are reports about intercalation of Al(III) cation\textsuperscript{19} and AlCl\textsubscript{4}\textsuperscript{−}\textsuperscript{18} anion, depending on the electrode active material, but in the case of MoO\textsubscript{3} the electrochemical results agree well with Al(III) intercalation. Cationic intercalation involves that aluminum firstly must lose its bond to Cl\textsuperscript{−} in the electrolyte solution and then to diffuse as Al(III) in MoO\textsubscript{3}.

The galvanostatic experiment shown in Figs. 2A, 2B was performed at low current density because the capacity at higher kinetics was lower (Fig. 2C), suggesting slow diffusion of aluminum in MoO\textsubscript{3}. The observed voltage-capacity curves exhibit several pseudplateaus (Fig. 2A), suggesting several oxidation states of molybdenum, structural changes of molybdate and a complex multiphase mechanism. The average voltage of the discharge-charge curves, regarded as the point of intersection of the charge and discharge lines, is ca. 0.9 V vs. Al. For the sake of comparison with other Al(III)-inserting materials in ionic liquid electrolyte we can cite that the average voltage reported for V\textsubscript{2}O\textsubscript{5} is ca 0.7 V\textsuperscript{16} and for VO\textsubscript{2} is ca. 0.5 V\textsuperscript{17} and for MoS\textsubscript{2} is also ca. 0.5 V\textsuperscript{19} Most of the discharge capacity is delivered between 1.1 and 0.5 V, being these values slightly higher than others reported for V\textsubscript{2}O\textsubscript{5}.\textsuperscript{16} Thus, our results on molybdate are consistent with previous reports on the electrochemical insertion of Al(III) in other host solids. On the other hand, the intercalation of chloroaluminates in graphite takes place at higher voltages values (2 V).\textsuperscript{15}

Voltage hysteresis between the charge and discharge is observed in the electrochemical experiments of molybdate (Fig. 2A). Although the overpotential depends on many factors, most probably it could be related to aluminum diffusion and structure transformation, as it will be discussed below taking into account the analysis of the aluminated molybdate.

In order to avoid or decrease side reactions, after the first two cycles of activation, a double limit (voltage and capacity) was simultaneously imposed for the electrochemical cycling experiment: voltage limits (0.4 and 1.98 V for discharge and charge, respectively) and capacity limit (100 mAh g\textsuperscript{−1} equivalent to Al\textsubscript{0.18}MoO\textsubscript{3}). The maximum observed reversible capacity is 100 mAh g\textsuperscript{−1} at 3 mA g\textsuperscript{−1} of current density. The capacity decreases after a few cycles (Fig. 2B). Other attempts to intercalate more aluminum into Al\textsubscript{x}MoO\textsubscript{3} drove to poorer electrochemical behavior (not shown). In Fig. 2C, only voltage limits were imposed, 0.1 V for the lower voltage limit and 2.1 V for the upper voltage limit and the current density was higher (10 mA g\textsuperscript{−1}) compared with Fig. 2A,B. It is observed that lower discharge and charge capacity values (around 30-15 mAh g\textsuperscript{−1}) are delivered because of the higher current density. Thus, low current density must be used to allow aluminum diffusion and to achieve higher capacities, but the side-reactions are enhanced at the lower current densities and consequently the capacity falls rapidly.

**Analysis of aluminated molybdate (Al\textsubscript{x}MoO\textsubscript{3}).—**In order to characterize the aluminated electrodes Al\textsubscript{x}MoO\textsubscript{3} and to explore the mechanism of the electrochemical reactions, electrodes were retrieved from the electrochemical cells and studied by EDS, XPS, NMR and XRD.

According to the EDS microanalysis results, the electrode after the first discharge has the experimental composition Al\textsubscript{0.14}MoO\textsubscript{3}, very close to the nominal composition Al\textsubscript{0.18}MoO\textsubscript{3}, based on the assumption that all the consumed charge in the electrochemical experiment is employed for aluminum intercalation. After the first discharge-charge cycle the experimental composition obtained from the EDS microanalysis is Al\textsubscript{0.10}MoO\textsubscript{3}. Consequently, the experimental change of the Al/Mo atomic ratio during the discharge/charge process agrees well with reversible accommodation of aluminum in molybdate.

The XPS results (Fig. 3) can be useful to monitor the changes of molybdenum oxidation states in the surface of the particles during the electrochemical cycling.\textsuperscript{26–28} For raw MoO\textsubscript{3} (Fig. 3a), the spectrum in the region of Mo 3d typical doublet of spin-orbit splitting (233.3–236.4 eV), most of the contribution to the deconvolution of the spectrum is due to Mo\textsuperscript{6+} (35.5%); Mo\textsuperscript{4+} (38.9%) is also observed. After the first discharge down to 96 mAh g\textsuperscript{−1} (equivalent to Al\textsubscript{0.18}MoO\textsubscript{3}), Mo\textsuperscript{6+} is the main component (40.7%), but Mo\textsuperscript{4+} (38.9%) is still observed and Mo\textsuperscript{5+} emerges (20.4%) (Fig. 3b). After the first discharge-charge cycle (Fig. 3c), the XPS of the retrieved electrode unveils the next oxidation states: Mo\textsuperscript{6+} (52.4%), Mo\textsuperscript{5+} (35.5%) and Mo\textsuperscript{4+} (12.1%). Aluminum was also detected by XPS (not shown), but the traces of electrolyte on the surface of the electrode make the overpotential depends on many factors, most probably it could be related to aluminum diffusion and structure transformation, as it will be discussed below taking into account the analysis of the aluminated molybdate.

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ambiguous the quantitative result. Irrespective of the fortuitous reaction of the surface with electrolyte and/or atmosphere, these spectra clearly show that the discharge-charge electrochemical cycling involves the reversible reduction of molybdenum atoms, at least in the particle surface. Obviously, these XPS results cannot unveil the details of the reaction mechanism in the inner part of the molybdate particles.

NMR spectroscopy is a valuable tool to study the local coordination of aluminum atom. Due to the limitations of the design of the electrochemical cell and the mass of sample needed for NMR measurements, we could record the spectrum only for a limited amount of intercalated aluminum at the beginning of the first discharge (Fig. 4a). The $^{27}$Al MAS NMR spectrum of slightly aluminated molybdate exhibits a narrow peak at +103 ppm and a broadened band at ca. -6 ppm (Fig. 4a). In contrast to that, the spectrum of MoO$_3$ soaked with electrolyte solution only show the peak at +103 ppm (Fig. 4b). According to the literature, octahedral coordination aluminum species are observed at ca. 0 ppm, tetrahedrally coordinated aluminum in the range from ca. 90 to ca.120 ppm, AlCl$_4$ at about +105 ppm, and the chemical shift of Al$_2$Cl$_7$ is $\delta = +116$ ppm.$^{29,30}$ The broadening of peak centered at – 6 ppm is indicative of low mobility into the host framework, compared to the narrow signal of the electrolyte at +103 ppm (Fig. 4b). Consequently, these NMR results are consistent with aluminum in octahedral sites in the reduced electrode due to intercalation of cationic Al(III) into molybdate.

The structural changes of the working electrodes were studied by ex-situ XRD (Fig. 5). The XRD pattern of uncycled MoO$_3$ electrode (Fig. 5a) agrees well with the JCPDS file number 05-0508 and Pbmm space group. The structure of layered MoO$_3$ is based on a sequence of double-layer sheets of distorted [MoO$_6$] octahedral sharing edges along one direction in the slabs (here “c”) and corners along the other direction (here “a”). The average crystallite size obtained from the broadening of the XRD reflections is $L = 440$ nm.

The average crystallite size obtained from the broadening of the XRD reflections is $L = 440$ nm. After the first discharge, new XRD reflections emerge at ca. 23.8, 25.4, 27.1 and 38.4° (Fig. 5b), and these reflections seem to come from the splitting of the reflections (110), (040), (021) and (060). The XRD results and Rietveld or Le Bail analysis agree well with the coexistence of two orthorhombic phases in the reduced electrode: raw MoO$_3$ and aluminated phase Al$_x$MoO$_3$. This aluminated phase is not Al$_2$(MoO$_4$)$_3$ (JCPDS file number 23-0764). Reflections of reduced molybdenum oxides (MoO$_2$, etc.) were not detected. During the charge process, the reflections of Al$_x$MoO$_3$ phase completely disappear (Fig. 5c), and then progressively emerge again during the second discharge (Figs. 5d, 5e). The reflections of raw MoO$_3$ never disappear, indicating that the core of the particles remain Al-free. These XRD results, all together with XPS and microanalysis results, let to conclude that aluminum reacts reversibly with MoO$_3$, at least in the region near the surface of the particles.

Two sites have been reported for intercalation of lithium in the framework of MoO$_3$:$^{31}$ the interlayer spacing between the Mo-O octahedron layers and the Mo-O octahedron intralayers. In our case,
we have tentatively found that the most adequate structure for the aluminated phase seems to be the space group Cmcm, more probably with Al(III) ions placed in the interlayer space. Nevertheless, taking into that only four new reflections of small intensity emerge for the aluminated phase, using the Rietveld method for fitting the XRD patterns could be a risky procedure of doubtful validity, and we cannot confirm the crystallographic site in which aluminum is located. More realistically, the Le Bail method using and orthorhombic cell is applied in Fig. 6. Although all the XRD patterns of the electrodes shown in Fig. 5 were fitted with LeBail method, only one discharged electrode is shown in Fig. 6 as an example. The Miller indexes of the main reflections ascribed to the aluminated phase are given in Fig. 6a, in which the whole XRD pattern and its fitting is shown. In Fig. 6b, the contribution of the platinum disc is simulated. The contributions of AlxMoO3 and MoO3 phases are shown in Fig. 6c and Fig. 6d, respectively. The coexistence of the Al-free MoO3 and AlxMoO3 phases in the reduced electrode can be easily observed, for example looking at the splitting of the reflection near 39°. The resulting lattice parameters for AlxMoO3 phase are a = 3.882(2), b = 14.09(2) and c = 3.731(4) Å. Thus, the intercalation of aluminum results in an increasing of the interlayer spacing (b axis) compared to Al-free MoO3, and the c-axis is also expanded. In contrast, the a-axis is slightly contracted. The values of the lattice parameters remained nearly unchanged independently of the cycle number for each of the phases (MoO3 and AlxMoO3). Compared to Al(III), insertion of chloroaluminate anions would result in larger volume expansion, like carbon materials.9,15

**Reaction mechanism.**—The electrochemical intercalation of aluminum into molybdite could be described according to the following half-reactions:

Positive electrode: \[\text{Mo}^{6+} + x\text{Al}^{3+} + 3\text{e}^- = \text{Al}_x \left(\text{Mo}^{(6-3x)+}\right)\text{O}_3\] [1]

Negative electrode: \[\text{Al}^{3+} + 7\text{AlCl}_4^- = 4\text{Al}_2\text{Cl}_7^- + 3\text{e}^-\] [2]

According to the experimental results, the Reaction 1 is reversible for \(x < 0.2\).

Alternatively to Reaction 1, one could think that a conversion reaction such as 3 could compete against the intercalation:

\[\text{MoO}_3 + 2x\text{Al} = x\text{Al}_2\text{O}_3 + \text{MoO}_{3-3x}\] [3]

where \(x < 1\). We cannot totally confirm whether Reaction 1 or 3 prevails. However, it is worth to note that the phases that would be expected for a conversion reaction (MoO2, Mo, Al2O3, etc.) were not observed by XRD. In addition, the changes of the slopes in the voltage curves (Fig. 2) suggest that the mechanism could be more complex. On the other hand, the XRD pattern of the electrode after 34 electrochemical cycles showed that the main structure of the molybdite was preserved, discarding structural collapse and/or corrosion.

Bearing in mind all the results shown above, more probably an intercalation of aluminum cation takes places near the surface of micrometric molybdite particles, while the inner core remains unaffected, similarly to the results found by Wang et al. using aqueous electrolyte.22 In addition, the intercalation of Al(III) near the surface of anatase particles has been proposed by other authors.32 Thus, more probably the initial intercalation of Al(III) in MoO3 forms a layer of AlxMoO3 which makes difficult further insertion and, consequently, the particle core remains Al-free (Fig. 7). The strong interactions Al-O in the layer of AlxMoO3 would affect to the aluminum diffusion, making difficult removing aluminum from the host and increasing the cell polarization, as it was observed in the hysteresis of the voltage curves (Fig. 2). In addition, a possibility to render this material more suitable for commercial aluminum batteries could be to optimize the microstructure and texture of the molybdite particles.

**Conclusions**

It is demonstrated here that aluminum can react reversibly with MoO3, using non-aqueous electrolyte and Al metal as counter electrode, with a maximum reversible capacity of about 100 mAh g\(^{-1}\), although capacity falls quickly in a few cycles. More probably, an intercalation reaction takes place and AlxMoO3 is formed in the region near the surface of the particles. Aluminated molybdite can be an orthorhombic phase, similarly to raw MoO3, with expanded interlayer spacing. The fine details of the intercalation mechanism could deserve further structural studies and theoretical calculations in future works. Molybdite could be potentially applied for aluminum batteries, but the electrolyte solution and the microstructure of MoO3 should be further improved.

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References

1. Y. Wang, R. Chen, T. Chen, H. Lv, G. Zhu, L. Ma, C. Wang, Z. Jin, and J. Liu, Energy Storage Mater., 4, 103 (2016).
2. A. Eftekhari and P. Corrochano, Sustainable Energy Fuels, 1, 1246 (2017).
3. S. K. Das, S. Mahapatra, and H. Lahan, J. Mater. Chem. A, 5, 6347 (2017).
4. F. Ambroz, T. J. Macdonald, and T. Nann, Adv. Energy Mater., 7, 1602093 (2017).
5. J. Xu, Y. Dou, Z. Wei, J. Ma, Y. Deng, Y. Li, and S. Dou, Adv. Sci., 4, 1700146 (2017).
6. Z. A. Zafar, S. Imtiaz, R. Alcántara, P. Lavela, and J. L. Tirado, Electrochim. Acta, 260, 798 (2018).
7. G. A. Elia, J. Marquardt, K. Hoepfner, S. Fantini, R. Lin, E. Knipping, W. Peters, J. F. Drillet, S. Passerini, and R. Hahn, Adv. Mater., 28, 7564 (2016).
8. Y. Zhang, S. Liu, Y. Ji, J. Ma, and H. Yu, Adv. Mater., 1706310 (2018).
9. X. F. Tong, F. Zhang, B. F. Ji, M. H. Sheng, and Y. B. Tang, Adv. Mater., 28, 9979 (2016).
10. L. D. Reed and E. Menke, J. Electrochem. Soc., 160, A915 (2013).
11. J. J. Auborn and Y. L. Barberio, J. Electrochem. Soc., 132, 598 (1985).
12. P. R. Gifford and J. B. Palmisano, J. Electrochem. Soc., 135, 650 (1988).
13. K. S. Mohandas, N. Sanil, M. Noel, and P. Rodriguez, Carbon, 41, 927 (2003).
14. M. C. Lin, M. Gong, B. G. Lu, Y. P. Wu, D. Y. Wan, M. Y. Guan, M. Angell, C. X. Chen, J. Yang, B. J. Hwang, and H. J. Dai, Nature, 520, 324 (2015).
15. S. Gu, H. Wang, C. Wu, Y. Bai, H. Li, and F. Wu, Energy Storage Mater., 6, 9 (2017).
16. W. Wang, B. Jiang, W. Xiong, H. Sun, Z. Lin, L. Hu, J. Tu, J. Hou, H. Zhu, and S. Jiao, Sci. Rep., 3, 3383 (2013).
17. W. Tang, X. Yuan, H. Wang, T. Zhao, and H. Liu, J. Power Sources, 384, 249 (2018).
18. B. Lee, H. R. Lee, T. Yim, J. H. Kim, J. G. Lee, K. Y. Chung, B. W. Cho, and S. H. Oh, J. Electrochem. Soc., 163, A1070 (2016).
19. V. Augustyn, J. Mater. Res., 32, 2 (2017).
20. E. Hatzikrianiotis, I. Samaras, and K. M. Paraskevopoulos, Ionics, 2, 29 (1996).
21. H. Wang, Z. Liu, X. Wang, X. Yuan, X. Wu, Y. Zhu, L. Fu, and Y. Wu, J. Mater. Chem. A, 4, 5115 (2016).
22. A. Bakkar and V. Neubert, Electrochem. Commun., 51, 113 (2015).
23. W. X. Song, X. B. Ji, Y. R. Zhu, H. J. Zhu, F. Q. Li, J. Chen, F. Lu, Y. P. Yao, and C. E. Banks, ChemElectroChem, 1, 871 (2014).
24. H. Lindström, S. Söldergren, A. Solbrand, H. Renstroem, J. Hjelm, A. Hagfeldt, and S. E. Lindquist, J. Phys. Chem. B, 101, 7717 (1997).
25. W. Li, F. Cheng, Z. Tao, and J. Chen, J. Phys. Chem. B, 110, 119 (2006).
26. H. N. Im, S. Y. Jeon, M. B. Choi, H. S. Kim, and S. J. Song, Ceram. Int., 38, 153 (2012).
27. E. G. Ilín, A. G. Beirakhov, Y. A. Teterin, K. I. Maslakov, and A. Y. Teterin, Inorg. Mater., 53, 602 (2017).
28. Z. Cerny, J. Machacek, J. Fusek, B. Casensky, O. Kriz, and D. G. Tuck, Inorg. Chem. Acta, 300–302, 556 (2000).
29. T. J. Boyle, N. L. Andrews, T. M. Alam, D. R. Tallant, M. A. Rodriguez, and D. Ingersoll, Inorg. Chem., 44, 5934 (2005).
30. T. Tsumura and M. Inagaki, Solid State Ionics, 184, 315 (2007).
31. A. Holland, R. D. Mckerracher, A. Cruden, and R. G. A. Wills, J. Appl. Electrochem., 48, 243 (2018).
32. A. M. L. Tirado, R. Alcántara, S. I. Lozano, J. L. Tirado, and S. Alonso, J. Electrochem. Soc., 165, A2994-A2999 (2018).