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Article

Comparative Study of Layered Manganese-based Oxides Doped with Iron. Titanium. and Aluminum: Positive Electrode Performance in K-Ion Battery Using an Ionic Liquid Electrolyte

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ABSTRACT

K-ion batteries (KIBs) are regarded as a viable option for large-scale electrical energy storage devices on account of their abundant potassium resources. Although layered P3-type manganese oxides and their derivatives have been studied as positive electrodes for KIBs, most of them use organic solvent-based electrolytes. We recently reported the improved performance of P3-type K_xMnO₂ positive electrode for KIBs with a highly safe ionic liquid electrolyte. In the present study, iron, titanium, and aluminum were doped into potassium manganese oxide positive electrode, and their charge-discharge properties were evaluated in the above ionic liquid electrolyte. The doped materials exhibited enhanced rate capabilities and cycling performances owing to their reduced surface resistance. The Al-doped material demonstrated the best cycling performance and highest discharge capacity, reaching 64.5 mAh g^{-1} with 92.8% capacity retention at 100 mA g⁻¹ over 100 cycles, owing to its low surface resistance. In addition, the structural stabilities of the Fe-, Ti-, and Al-doped materials during the charge-discharge process were confirmed through reversible crystal structural evolution observed via ex-situ X-ray diffraction. Finally, a stable cycling performance was also demonstrated in a K-ion full cell composed of an Al-doped potassium manganese-oxide positive electrode and a graphite negative electrode.

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Keywords : K-ion Battery, Ionic Liquid, Manganese-based Positive Electrode, Doping

1. Introduction

Rechargeable Li-ion batteries (LIBs) have been popularly used as energy storage systems in various electronic devices because of their high energy density and output voltage.¹ As LIBs are increasingly being used for electric vehicles and stationary energy storage, there is a growing concern about the increasing cost and potential scarcity of Li and Co resources.² To ensure a sustainable energy supply, significant efforts have been directed toward developing alternative battery technologies, such as Na-ion batteries (NIBs) and K-ion batteries (KIBs). Sodium and potassium are abundant, ranking sixth (2.36 wt%) and seventh (2.09 wt%) among elements in the Earth's crust, respectively.³ Compared to NIBs, KIBs have gained more attention due to the ability to use commercially available graphite as a negative electrode. Furthermore, K⁺/K exhibits a standard redox potential of -2.93 V (vs. the standard hydrogen electrode (SHE)) which is similar to that of Li⁺/Li (-3.04 V vs. SHE) and lower than that of Na⁺/Na (-2.71 V vs. SHE),^{4,5} enabling the development of higher-voltage KIBs. However, the larger atomic radius of K⁺ (1.38 Å) than those of Na⁺ (1.06 Å) and Li⁺ (0.76 Å),^{6–8} presents challenges for KIBs. Upon K⁺ intercalation and deintercalation, the positive electrode materials undergo irreversible phase transitions and significant structural deterioration, resulting in poor cycling performance. In the last decade, Mn-based layered oxides have been explored as positive electrode materials for KIBs,⁹⁻¹³ owing to their

excellent properties such as high theoretical capacity, non-toxicity, low cost, and abundance. Synthesized Mn-based layered transition metal oxides, $K_x MnO_2$ (0 < x < 1), can be categorized into P2and P3-type according to the stacking order of the MnO₆ and K⁺ layers, where K⁺ occupies the prismatic coordination environment.¹¹ The distorted P2-K_{0.3}MnO₂ positive electrode material was first demonstrated with a discharge capacity of approximately 65 mAh g^{-1} at 27.9 mA g $^{-1}$ between 1.5 and 3.5 V.¹² Subsequently, P3-K_{0.5}MnO₂ also reportedly exhibited a capacity of approximately 100 mAh g^{-1} at a current density of 5 mA g $^{-1}$ in the voltage range of 1.5-3.9 V owing to the reversible phase transition.⁹ A series of P3- K_x MnO₂ (0 < x < 1) compounds was doped with different elements, such as Mg, Ni, Al, and Fe, to improve their electrochemical performances. These dopants enhance performance by mitigating the Jahn-Teller effect of Mn³⁺, or improving the structural stability, layer spacing, and conductivity.¹⁴⁻¹⁷ Furthermore, P3- $K_{0.45}Mn_{1-x}Fe_xO_2$ (0.1 $\leq x \leq 0.5$) materials with different Fe contents were synthesized and their electrochemical performance for KIBs was evaluated using an organic solvent electrolyte. A 20 wt% Fe-doped K_{0.45}MnO₂ electrode demonstrated the highest specific capacity of 104.6 mAh g^{-1} at 20 mA g^{-1} between 1.5 and 4.0 V.¹⁷

Adopting organic solvent-based electrolytes in LIBs can potentially cause safety issues because of their volatile and flammable nature. Ionic liquids (ILs), also known as room-temperature molten salts, are considered safe alternatives to traditional organic solventbased electrolytes owing to their wide voltage window, moderate ionic conductivity, as well as negligible volatility and nonflammability.¹⁸ We have previously focused on the application of ionic liquids in KIBs.^{19–22} In M[FSA]–[C₃C₁pyrr][FSA] (M = Li, Na, K; $FSA = bis(fluorosulfonyl)amide, C_3C_1pyrr = N-methyl-N-propyl$ pyrrolidinium) ionic liquids, the redox potential of the K^+/K couple is more negative than that of Li⁺/Li by 0.24 V and Na⁺/Na by 0.35 V

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at 298 K when the molar fraction of M[FSA] (x(M[FSA])) is equal to 0.20.¹⁹ The lower redox potential of K⁺/K is beneficial for operating KIBs at a higher voltage and mitigating the risks of alkali-metal deposition. Furthermore, transition metal oxide positive electrodes such as KFeO₂ were confirmed to facilitate the reversible intercalation and deintercalation of K⁺ in the K[FSA]–[C₃C₁pyrr][FSA] ionic liquid electrolyte.²¹ Additionally, the excellent electrochemical behaviors of negative electrode materials such as graphite for KIBs in this electrolyte have also been reported in our previous studies.²⁰

The enhanced charge-discharge performance of P3-K_{0.46}MnO₂ was recently reported using the K[FSA]-[C₃C₁pyrr][FSA] ionic liquid electrolyte,²² possibly contributed by the formation of stable CEI layer²³ and suppression of the Mn dissolution²⁴ upon the intercalation and deintercalation of K⁺. In the present study, aiming to further improve the electrochemical performance of P3- $K_{0.46}$ MnO₂, we explored doping it with several elements such as Fe, Ti, and Al, and investigated their charge-discharge behaviors in the same K[FSA]-[C₃C₁pyrr][FSA] ionic liquid electrolyte. Electrochemical impedance spectroscopy (EIS) was used to investigate the mechanism behind the enhanced performance resulting from the partial substitution of Mn with Fe, Ti, and Al. The crystal structural evolutions during K⁺ intercalation and deintercalation were analyzed using ex-situ X-ray diffractometry. Finally, the full-cell performance of the Al-doped K_{0.46}MnO₂ positive electrode was examined in combination with the graphite negative electrode.

2. Experimental

2.1 Synthesis of materials

Layered P3-K_{0.46}MnO₂ and 5 wt% Fe-, Ti-, and Al-doped samples were fabricated via a solid-state method and denoted as KMO, KMFO, KMTO, and KMAO, respectively. All reagents were of analytical pure and used directly as supplied without any additional purification. First, mixtures of K₂CO₃ (Sigma-Aldrich, 99.99 % purity), Mn₂O₃ (Sigma-Aldrich, 99.9 % purity), and dopant (Fe₂O₃ (FUJIFILM Wako Pure Chemical Corp., 99.9% purity), TiO₂ (Sigma-Aldrich, 99.8% purity), or Al₂O₃ (Sigma-Aldrich, 99.99% purity)) with a molar ratio of 0.52:0.95:0.05 were homogenized by grinding with an agate mortar, respectively. This ratio corresponds to a K2CO3 excess of approximately 15% compared to the stoichiometric amount of the target material, and was optimized by considering K₂CO₃ vaporization. The mixtures were calcined in a box furnace at 1123 K for 15 h under air exposure. To prevent moisture contamination at room temperature, the assynthesized materials were transferred to an open dry chamber after cooling to 573 K. They were then ground in a mortar for 20 min before being stored in an Ar-filled glove box (H_2O , $O_2 < 0.5$ ppm) until further use.

2.2 Material characterization

Quantitative elemental analysis of the as-synthesized materials was performed using inductively coupled plasma atomic emission spectrometry (ICP-AES; Hitachi, Spectroblue). A scanning electron microscopy (SEM; Phenom Pro Generation 5, Thermo Fisher Scientific) and an energy-dispersive X-ray spectroscopy (EDS; SE1200-8001, Thermo Fisher Scientific) were used to determine the morphologies and elemental distributions of the as-synthesized materials after the samples were coated with Au to improve the conductivity. An ex-situ X-ray diffractometer (XRD; Ultima IV, Rigaku) with CuK α radiation ($\lambda = 1.5418$ Å) was used to record the X-ray diffraction patterns of the as-synthesized powder materials and electrodes over the 2θ ranges of 10–80° and 10–40° at a scan rate of 2° min⁻¹, respectively.

2.3 Electrochemical measurements

Charge-discharge performances of the positive electrodes were

evaluated using CR2032-type two-electrode coin cells with K metal (Sigma-Aldrich, 98 % purity) as the counter electrode and two-ply glass fiber (Whatman, GF/A, thickness: 260 µm) as the separator. Active materials, acetylene black, and poly(tetrafluoroethylene) were mixed at a weight ratio of 85 : 10 : 5 in an Ar-filled glove box, and the resultant films were then pressed onto the surface of an Al mesh (diameter: 10 mm) to fabricate the working electrodes. The average loading mass of the active materials was about 8.5 mg cm⁻². The K[FSA]–[C₃C₁pyrr][FSA] electrolyte (x(K[FSA]) = 0.20) was prepared by dissolving K[FSA] salt (Nippon Shokubai Co., Ltd., \geq 99 % purity) in [C₃C₁pyrr][FSA] ionic liquid (Kanto Chemicals Co., Ltd.). Prior to the cell assembly, the electrodes were vacuum-impregnated with separators at 333 K overnight in the K[FSA]–[C₃C₁pyrr][FSA] ionic liquid electrolytes.

For the ex-situ X-ray diffraction (XRD), the half-cells at various charge–discharge states were disassembled in the glovebox, and the positive electrodes were transferred and measured using an airtight holder to avoid contact with moisture owing to the hygroscopic nature of the transition metal oxide. A potentiostat (VSP, Biologic Co.) was used to perform electrochemical impedance spectroscopy (EIS) measurements. Because K metal has a large resistance, we used symmetric coin cells containing two equivalent positive electrodes to measure the resistance of a single positive electrode. EIS measurements were performed at an amplitude of 20 mV over a frequency range of 200 kHz to 100 mHz, following a 10-minute stabilization of the symmetric coin cells at 0 V.

Finally, the K-ion full cell was operated in a two-electrode coin cell at a current rate of 40 mA g^{-1} between 1.5 and 4.0 V using an Al-doped KMO positive electrode and graphite negative electrode. The graphite electrode was fabricated by mixing graphite powder (SNO-3, SEC carbon, particle size: 3 µm) and sodium carboxyl methylcellulose (CMC, #2200, Daicel Miraizu Ltd.) at a weight ratio of 90:10 and coating the resultant slurry on an Al foil current collector (diameter: 10 mm). In this study, the initial irreversible capacities of the positive and negative electrodes were eliminated by pre-cycling in different coin cells with K metal counter electrodes as follows. The KMAO positive electrode was pre-cycled at 40 mA g^{-1} between 1.5 and 4.0 V for 5 cycles, and the graphite negative electrode was pre-cycled at 40 mA g^{-1} for 3 cycles and then at 75 mA g^{-1} for another 3 cycles within a voltage range of 0.01–1.5 V. The N/P ratio of the full cell was approximately 1.14 (positive electrode: loading mass of 1.86 mg (8.09 mg cm⁻²) and specific capacity of $95 \,\text{mAh}\,\text{g}^{-1}$; negative electrode: loading mass of 1.06 mg (1.35 mg cm^{-2}) and specific capacity of 190 mAh g^{-1}). The specific capacity and current density of the full cell were calculated based on the mass of the KMAO positive electrode material. A potentiostat (580-type battery cycler, Scribner Associations, Inc.) was used to perform charge-discharge tests on the half and full cells.

3. Results and Discussion

The exact chemical compositions of the KMO, KMFO, KMTO, and KMAO powders were determined via ICP-AES (Table 1). The K : Mn : dopant (Fe, Ti, and Al) atomic ratios were 0.46 : 0.95 :0.05, 0.46 : 0.95 : 0.05, and 0.43 : 0.95 : 0.04, respectively, whichagree well with the designed ones. The crystal structures of the assynthesized KMFO, KMTO, and KMAO were studied via powderXRD analyses; the XRD pattern of KMO is provided as a reference $in Figs. 1a and 1b. The hallow pattern located in the range <math>10-35^{\circ}$ originated from the airtight holder. The XRD patterns of all the samples are identical to the calculated diffraction patterns of P3-K_{0.5}MnO₂ with the *R*3*m* space group.²⁵ Figure 1c shows a schematic diagram of the layered P3-type crystal structure. The main peaks of the KMFO, KMTO, and KMAO pristine electrodes at approximately 13.8° were assigned to the 003 diffraction. The enlarged

 Table 1.
 Elemental compositions of KMO, KMFO, KMTO, and KMAO powders obtained from ICP-AES.

Sample	Measured atomic ratio of synthesized powder		
	K	Mn	dopant
КМО	0.46	1	_
KMFO	0.46	0.95	0.05
KMTO	0.46	0.95	0.05
KMAO	0.43	0.95	0.04

view of the 003 diffraction (Fig. 1b) indicates that angle shifts in the XRD diffraction patterns were nearly non-existent owing to the limited amount of dopant and similar atomic radius of Mn, Fe, Ti, and Al.²⁶ The XRD and ICP-AES results indicate the successful synthesis of the target material. In addition, Fig. S1 shows the XRD patterns of the KMFO, KMTO, and KMAO powders measured after exposure to air for 5 h. Similar to the KMO powder,²² these powders demonstrate a lower diffraction-angle shift of the main peaks at approximately 13.9° and 27.9°. Unknown peaks appear in the region of 35°-68°, indicating that the Fe-, Ti-, and Al-doped KMO also show sensitivity to moisture at room temperature. Figures S2, S3, and S4 show the morphologies, elemental compositions, and distributions of the as-synthesized KMFO, KMTO, and KMAO powders obtained by the SEM and EDS analyses. The KMFO, KMTO, and KMAO powders are characterized with similar morphologies and consist of primary particles (1-2 µm) and secondary particles (5-10 µm). Although EDS is difficult to accurately determine the quantitative amount of element, EDS results indicate that the KMFO, KMTO, and KMAO powders exhibit atomic ratios of 0.49: 0.95: 0.06 for K: Mn: Fe, 0.45: 0.95:0.08 for K: Mn: Ti, and 0.46:0.95:0.04 for K: Mn: Al, which agrees well with the ICP-AES results. Furthermore, Figs. S2d-S2g, S3d-S3g, and S4d-S4g confirm the homogeneous elemental distributions of K, Mn, Fe, Ti, Al, and O in each sample with EDS mappings.

The K⁺ storage performances of the KMO, KMFO, KMTO, and KMAO positive electrodes were evaluated between 1.5 and 4.0 V in half-cells with K metal as the counter electrode. Figures 2a–2e present the rate performances of KMO, KMFO, KMTO, and KMAO electrodes at current densities ranging from 20 to 500 mA g⁻¹. All the electrodes exhibit similar charge–discharge curves, indicating no significant differences in the fundamental reaction mechanism among these materials. It should be noted that the rate capability and cycle performance of KMO (Fig. 2a) were obtained from the same system as in the previous paper,²² but different data. The

obtained data in the present and previous studies are quite similar, which indicates good reproducibility. The theoretical capacity of $K_{0.46}MnO_2$ was calculated to be 255 mAh g⁻¹, assuming the reaction in the compositional range of $0 \le x \le 1$ for K_xMnO_2 . The KMO positive electrode delivers an initial charge and discharge capacity of 65.1 and 126 mAh g⁻¹, corresponding to an initial coulombic efficiency of 194%. The initial charge and discharge capacities of KMO correspond to a deintercalation of 0.25 K⁺ and intercalation of 0.49 K⁺. The reaction formulas are as follows:

(1st charge) $K_{0.46}MnO_2 \rightarrow K_{0.21}MnO_2 + 0.25K^+ + 0.25e^-$ (1)

(1st discharge) $K_{0.21}MnO_2 + 0.49K^+ + 0.49e^- \rightarrow K_{0.70}MnO_2$ (2)

The KMO electrode delivers average discharge capacities of 113, 91.2, 73.3, 65.7, 52.5, and 33.4 mAh g^{-1} over 5 cycles at 20, 40, 80, 100, 200, and 500 mA g⁻¹. Regarding the Fe-, Ti-, and Al-doped KMO electrodes, the initial discharge capacities for KMFO, KMTO, and KMAO are 124, 125, and 139 mAh g⁻¹ with initial coulombic efficiencies of 212%, 227%, and 211%, respectively, and their discharge capacities decrease to 109-112 mAh g⁻¹ in five cycles, similar to that of KMO (107 mAh g^{-1}). Although the KMO, KMFO, KMTO, and KMAO electrodes demonstrate nearly the same capacities at a low current density of 20 mA g⁻¹, enhanced rate capabilities are observed for the doped materials at higher current densities (see Fig. 2e). For example, the KMAO electrode exhibits reversible discharge capacities of 122, 96.8, 79.0, 73.5, 59.0 and $39.2 \text{ mAh } \text{g}^{-1}$ at 20, 40, 80, 100, 200, and $500 \text{ mA } \text{g}^{-1}$. In addition, a discharge capacity of 105 mAh g⁻¹ is maintained after resetting to 20 mA g⁻¹, indicating the excellent structural stability of the KMAO electrode. Figure 2f presents the cycling performances of the KMO, KMFO, KMTO, and KMAO electrodes at a current density of 100 mA g⁻¹ for 100 cycles; their charge–discharge curves are shown in Fig. S5. All the KMO and doped-KMO positive electrodes exhibit similar charge-discharge curves, the shapes of which are retained even after 100 cycles, indicating that their robust structures can stably facilitate the reversible intercalation and deintercalation of K⁺ ions. For the KMFO electrode, a reversible capacity of 60.4 mAh g^{-1} is maintained after 100 cycles operated at 100 mA g $^{-1}$, which corresponds to 89.7 % of the initial discharge capacity. The KMTO electrode exhibits a current density of 62.2 mAh g^{-1} with a capacity retention of 85.7 % after 100 cycles. Comparatively, the KMAO electrode demonstrates the highest discharge capacity of 64.5 mAh g^{-1} with a capacity retention of 92.8 % after 100 cycles. All the Fe-, Ti-, and Al-doped KMO electrodes show higher specific capacities than that of the KMO electrode, which delivers a discharge capacity of $50.6 \,\mathrm{mAh}\,\mathrm{g}^{-1}$ with a capacity retention of 87.6%. These results indicate the enhanced charge-discharge properties of the doped KMO materials.



Figure 1. (a) XRD patterns and (b) their enlarged views of KMO, KMFO, KMTO, and KMAO powders; (c) schematic diagram of the P3-type crystal structure.

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Figure 2. Charge–discharge curves of the positive electrodes: (a) KMO, (b) KMFO, (c) KMTO, and (d) KMAO. (e) Summary of the rate capability at various current densities ranging from 20 to 500 mA g^{-1} . (f) Summary of the cycle performance at a current density of 100 mA g^{-1} in the voltage range of 1.5-4.0 V. The data of (a) was obtained from the same system as in the previous paper and were almost identical to the data shown in Fig. 2a in Ref. 22.

To further investigate the doping effects on the KMO as positive electrode for KIBs, an EIS analysis was performed before cycling using symmetric cells (Fig. 3). The Nyquist plots (Fig. 3a) present the relationship between the real and imaginary parts of the impedance, and the Bode plots (Figs. 3b and 3c) indicate the phase shifts and magnitude changes in the frequency ranging from 200 kHz to 100 mHz. According to the Nyquist plots (Fig. 3a), the KMO, KMFO, KMTO, and KMAO electrodes show similar EIS spectra, with a semicircle in the high-frequency region over approximately 6 Hz, and a straight line in the low-frequency region below approximately 6 Hz. The semicircle region typically corresponds to the surface resistance, which is mainly attributed to the charge-transfer resistance in these symmetric cells. The EIS spectrum indicates the charge-transfer resistance of the KMO electrode is reduced by Fe, Ti, and Al doping, where the KMFO and KMTO electrodes exhibit similar surface resistances, but higher than that of the KMAO electrode. The lowest surface resistance of the KMAO electrode is responsible for the best cycling performance. although the KMTO and KMFO electrodes also show enhanced cycling performances compared with the KMO electrode. The KMO, KMFO, KMTO, and KMAO electrodes exhibit similar Bode

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plots (Figs. 3b and 3c). The phase values of the impedance decrease as the frequency increases to approximately 6 Hz (Fig. 3b), corresponding to a straight line in the Nyquist plot in the lowfrequency region. In the high-frequency region ranging from approximately 6 Hz to 200 kHz, the phase values increase and then decrease, which is consistent with the semicircles of the Nyquist plots. Additionally, the relationship between the impedance magnitude and frequency (Fig. 3c) shows a slight decrease in the impedance as the frequency increases up to approximately 6 Hz, corresponding to a straight line in the Nyquist plot. Subsequently, the impedance further decreases as the frequency increases, and then stabilizes at a plateau in the frequency region above 10^5 Hz, corresponding to the semicircle in the Nyquist plot at high frequencies. Similar to that shown in the Nyquist plots, the KMFO and KMTO electrodes also exhibit a lower impedance than that of the KMO electrode; the KMAO electrode has the lowest impedance among the electrodes.

To elucidate the K^+ storage mechanism and the evolutions in the crystal structures of the KMFO, KMTO, and KMAO electrodes upon the intercalation and deintercalation of K^+ ions, we used exsitu X-ray diffraction for the different charge–discharge states of the



Figure 3. (a) Nyquist and (b–c) Bode plots of the KMO/KMO, KMFO/KMFO, KMTO/KMTO, and KMAO/KMAO symmetric cells.

1st cycle at a current density of 20 mA g^{-1} in the voltage range of 1.5–4.0 V (Figs. 4 and S6). Changes in the XRD pattern of the KMO electrode detected in our previous study²² were used for comparison. Figure S7 compares the XRD patterns and their enlarged views at the pristine, charged, and discharged stages of

the 1st cycle, all of which exhibit XRD pattern evolutions similar to those of KMO²² during the charge and discharge processes. Upon charging to 3.9 V, the 003 diffraction peak of the electrodes shift slightly to a lower angle, because the formation of potassium vacancies causes the increases in the Coulombic repulsion between the oxygen slabs and the interlayer spacing (along the c axis). Accompanied by the disappearance of the 003 diffraction peaks, unknown peaks appear at approximately 10.8°, 21.9°, and 36.3° upon charging to 4.0 V. Due to the concern that air contamination may lead to the formation of these unknown peaks, we further investigated the effect of air exposure on structural changes of positive electrode materials. Figure S8 compares the XRD patterns of pristine KMAO powder and a KMAO positive electrode charged to 4.0 V before and after exposure to air for 5 h. After the air exposure, a broad peak appears in the range of 12.0-12.5° in the XRD pattern of the charged KMAO electrode, which is similar to the peak observed in the air-exposed pristine KMAO powder. Thus, the new peak around 12.5° is considered to be attributable to hydrated phases. After the exposure to air, both the pristine KMAO powder and the KMAO positive electrode charged to 4.0 V show different XRD patterns compared to those obtained using an airtight holder, suggesting that the airtight holder effectively prevents air contamination. During the discharge process, the unknown peaks of the KMFO, KMTO, and KMAO electrodes disappear at 3.0 V. We previously estimated that Mn migrated reversibly into the K layer which caused a phase transition and the reversible formation of unknown patterns.²² Upon further discharging to 1.5 V, the 003 diffraction peaks of the KMFO, KMTO, and KMAO electrodes shift to a higher angle as the Coulombic repulsion between the oxygen slabs decreases with the intercalation of the K⁺ ions. The diffraction patterns in the fully discharged state are similar to those of the pristine electrodes, indicating the excellent structural stabilities of the KMFO, KMTO, and KMAO electrodes.

Finally, the full-cell performance of the KMAO positive electrode was demonstrated with graphite as the negative electrode; its charge–discharge curves and cycle performance are displayed in Fig. 5. The KMAO positive electrode and graphite negative electrode were pre-cycled in half-cells to remove their irreversible capacities before assembling the full cell. Figure S9 presents the pre-cycle charge–discharge curves of the KMAO positive electrode, which delivers a reversible capacity of approximately 95 mA g⁻¹ in the half-cell, as well as the graphite negative electrode, which delivers reversible discharge capacities of 210 mAh g⁻¹ at 40 mA g⁻¹ and 190 mAh g⁻¹ at 75 mA g⁻¹. The full cell exhibits a reversible discharge capacity of 77.7 mAh g⁻¹ at 40 mA g⁻¹ in the voltage range of 1.5–4.0 V after 30 cycles, corresponding to a capacity retention of 95.2 %. This result indicates the stable charge and discharge performance of the KMAO full cell.



Figure 4. Ex-situ XRD patterns of (a) KMO,²² (b) KMFO, (c) KMTO, and (d) KMAO electrodes with varying charge–discharge states during the 1st cycle conducted at a current density of 20 mA g^{-1} in the voltage range of 1.5-4.0 V. KMO data were reproduced from Ref. 22.



Figure 5. Full-cell performance of the KMAO positive electrode with graphite as a negative electrode at a current density of 40 mA g^{-1} in the voltage range of 1.5-4.0 V. (a) Galvanostatic charge–discharge profiles, and (b) cycle performance.

4. Conclusions

Fe-, Ti-, and Al-doped layered P3-type potassium manganese oxides were successfully synthesized via a solid-state method. Their enhanced electrochemical performance as a positive electrode for Kion batteries was studied using an K[FSA]-[C₃C₁pyrr][FSA] ionic liquid electrolyte and compared with that of the conventional potassium manganese oxide. Owing to the reduced surface resistance, the Fe-, Ti-, and Al-doped K_{0.46}MnO₂ positive electrodes exhibited enhanced rate capabilities and cyclabilities. The Al-doped K_{0.46}MnO₂, which showed the lowest surface resistance, exhibited the best cycling performance with a discharge capacity of $64.5\,mAh\,g^{-1}$ and a capacity retention of 92.8 % at $100\,mA\,g^{-1}$ in the voltage range of 1.5-4.0 V over 100 cycles. Fe-, Ti-, and Aldoped K_{0.46}MnO₂ exhibited excellent structural stabilities with reversible crystal evolutions upon K⁺ intercalation and deintercalation. In addition, the full-cell performance of the Al-doped $K_{0.46}$ MnO₂ positive electrode with graphite as the negative electrode was confirmed to have a stable cyclability.

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CRediT Authorship Contribution Statement

- Kai Jiao: Data curation (Equal), Investigation (Lead), Methodology (Equal), Validation (Equal), Writing original draft (Lead)
- Takayuki Yamamoto: Conceptualization (Lead), Data curation (Equal), Funding acquisition (Lead), Methodology (Equal), Supervision (Equal), Validation (Equal), Writing – review & editing (Equal)
- Toshiyuki Nohira: Data curation (Equal), Methodology (Equal), Supervision (Equal), Validation (Equal), Writing review & editing (Equal)

Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare that they have no known competing financial interests.

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