

Short communication

# Synthesis and electrochemical properties of spherical spinel $\text{Li}_{1.05}\text{M}_{0.05}\text{Mn}_{1.9}\text{O}_4$ (M = Mg and Al) as a cathode material for lithium-ion batteries by co-precipitation method

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## Abstract

Cation (Mg and Al)-substituted spinel were synthesized using metal oxide precursor by co-precipitation method. XRD revealed that the prepared substituted spinel has spinel structure with  $Fd\bar{3}m$  space group. In order to compensate the decreased initial capacity of cation-substituted spinel, partial anion (F) substitution was also carried out. The cycling performance of all the substituted spinel was improved, compared to the  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  at 55 °C.  $\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  showed better capacity retention than the other substituted spinels. Both cation and anion substitution appeared to be effective for improving the cycling performance of spinel material at elevated temperature.

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**Keywords:** Lithium-ion battery; Cathode; Spinel; Co-precipitation; Substitution

## 1. Introduction

Spinel  $\text{LiMn}_2\text{O}_4$  and its derivatives have been studied as one of the most attractive cathode materials for lithium-ion batteries because of their low cost, and non-toxicity, compared with  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ . However,  $\text{LiMn}_2\text{O}_4$  exhibits severe capacity fading problem at the elevated temperature (above 40 °C) as well as at ambient temperature. The mechanism for capacity fading of  $\text{LiMn}_2\text{O}_4$  during cycling is not clearly identified yet, and several possible mechanisms are suggested: such as the dissolution of manganese into electrolyte [1–3], Jahn–Teller distortion [1,4], and change in crystal lattice arrangement with cycling [5], and so on.

In an effort to overcome capacity fading, the partial substitution of manganese ions with the various transition metals such as Co, Ni, Fe, Cr, Zn, and Cu [6–11] have been tried. Reducing the amount of  $\text{Mn}^{3+}$  ion in the structure by the cation substitution was approved to be one of successful approaches to prevent Mn dissolution during cycling. Especially, partial Al doping on

the 16d Mn site showed the improved cycling performances at room temperature and at elevated temperature [12,13].

In this study, we report the preparation and electrochemical properties of  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-x}\text{O}_4$  (M = Al and Mg;  $x=0$  and 0.05) using pre-formed  $(\text{M-Mn})_3\text{O}_4$  precursor by a hydroxide co-precipitation method. Also anion (F) doping on cation-doped spinel was tried to observe the effect of both cation and anion doping on the cycling performance.

## 2. Experimental

$[\text{M}_x\text{Mn}]_3\text{O}_4$  (M = Mg and Al;  $x=0$  and 0.05) powder were synthesized by co-precipitation method. An aqueous solution of  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ , and various metal solutions ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{MgSO}_4$ ) with a concentration of 2.0 mol  $\text{L}^{-1}$  were pumped into a continuously stirred tank reactor under air atmosphere. Simultaneously, a NaOH solution (aq) of 4.0 mol  $\text{L}^{-1}$  and a proper amount of  $\text{NH}_4\text{OH}$  solution (aq) as a chelating agent were separately fed into the reactor.

Initially manganese hydroxide was formed, and then the formed manganese hydroxide was oxidized into manganese oxide under air atmosphere. An irregular shaped particle gradually changed into spherical particles by vigorous stirring. The

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obtained  $(M_xMn)_3O_4$  ( $M = Al$  and  $Mg$ ;  $x = 0$  and  $0.05$ ) powder were dried in  $110^\circ C$  for 12 h to remove adsorbed water. Finally, precursor  $(M_xMn)_3O_4$  ( $M = Al$  and  $Mg$ ;  $x = 0$  and  $0.05$ ) mixture containing an excess amount of  $LiOH \cdot H_2O$ , were pre-heated to  $500^\circ C$  for 5 h in oxygen, and subsequently heat treated for 15 h at  $800^\circ C$  in a furnace under oxygen purging. For synthesis of  $Li_{1.05}M_xMn_{1.95-(x+y)}O_{4-y}F_y$  ( $x = 0.1$  and  $y = 0.05$ ), the stoichiometric amount of  $LiF$  was added.

Powder X-ray diffraction (Rigaku, Rint-2000) using  $Cu K\alpha$  radiation was used to identify crystalline phase of the prepared powders at each stage. The morphology of prepared powders was also observed using scanning electron microscopy (SEM, JSM-6340F, JEOL). The chemical compositions of the final powders were analyzed with an atomic absorption spectroscopy (AAS, Vario 6, Analyticjena).

Charge–discharge tests were performed with coin type cell (CR2032) by applying a constant current density of  $0.4 mA cm^{-2}$  at  $55^\circ C$ . The coin cells comprised of the prepared powder as positive electrode, lithium foil anode and an electrolyte having 1 M  $LiPF_6$  in a 1:1 vol.% of ethylene carbonate (EC) and diethyl carbonate (DEC) (Cheil Industries Inc., Korea). The micro-porous polypropylene separator was used in these cells. The cell preparation was carried out in the Ar-filled dry box. The cells were charged and discharged in the voltage range of 3.4–4.3 V at a constant current density of  $0.4 mA cm^{-2}$  at  $55^\circ C$ . Cycle life test was also carried out in the same voltage range of 3.4–4.3 V at  $55^\circ C$ .

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the prepared  $(M-Mn)_3O_4$  ( $M = Al$  and  $Mg$ ) powder. Significant impurity phases were not observed for Mg-doped and Al-doped  $Mn_3O_4$ , implying that the dopants are incorporated into the spinel structure without distortion of the host structure.

The SEM images shown in Fig. 2 show that the prepared  $(M-Mn)_3O_4$  ( $M = Mg$  and  $Al$ ) have a spherical morphology. It is interesting that the average particle size of the prepared metal oxide slightly varies with the dopants (Mg and Al). Among them, Mg-doped  $Mn_3O_4$  has a larger particle size than that of  $Mn_3O_4$ .

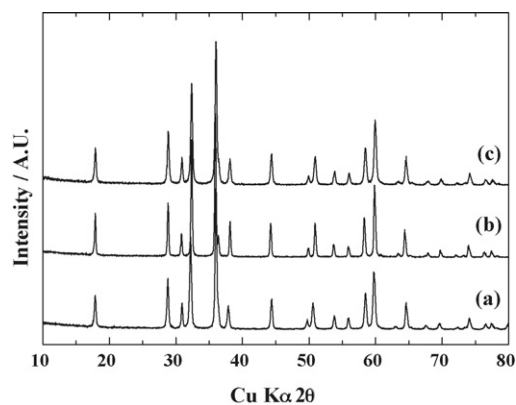


Fig. 1. Powder X-ray diffraction patterns of  $(M-Mn)_3O_4$ : (a)  $Mn_3O_4$ , (b)  $M=Mg$ , and (c)  $M=Al$  synthesized *via* co-precipitation method (dried at  $110^\circ C$ ).

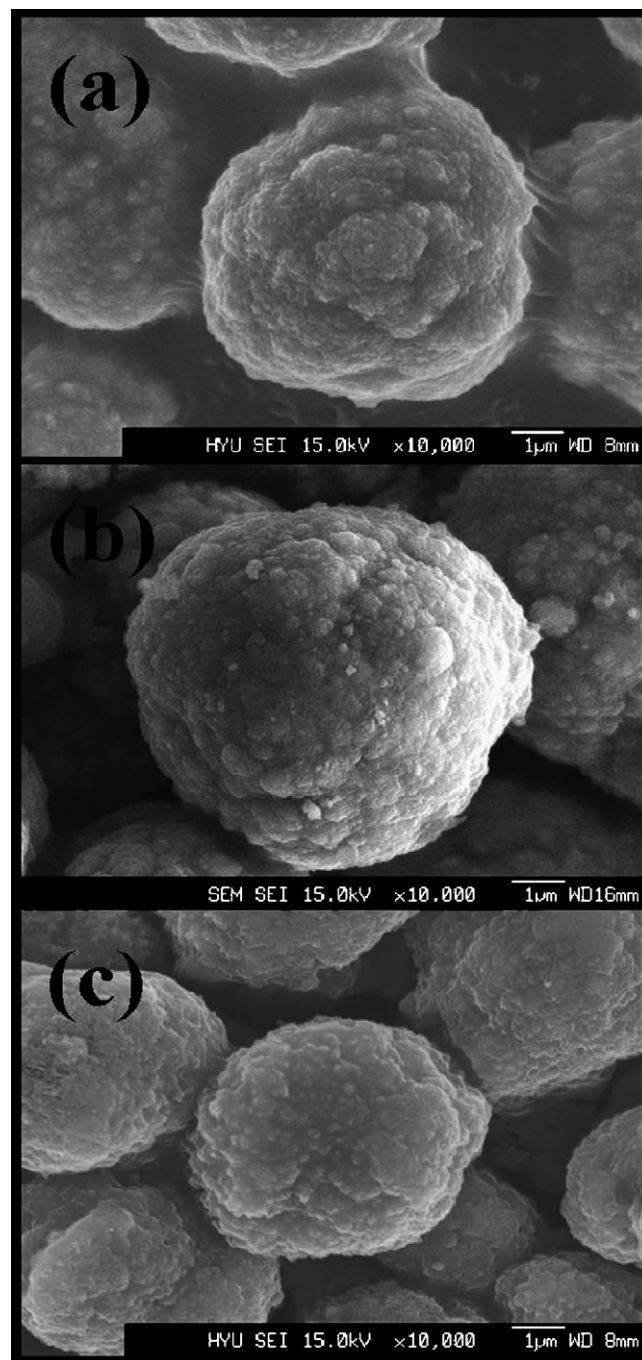


Fig. 2. SEM images of  $(M_xMn)_3O_4$  precursor: (a)  $Mn_3O_4$ , (b)  $M=Mg$ , and (c)  $Mn=Al$ .

On the other hand, the average particle size of Al-doped  $Mn_3O_4$  is smaller than  $Mn_3O_4$ .

Fig. 3 shows the XRD patterns of the  $Li_{1.05}M_xMn_{1.95-(x+y)}O_{4-y}F_y$  ( $M = Mg$  and  $Al$ ;  $x = 0, 0.05$  and  $0.1$ ;  $y = 0$  and  $0.05$ ) samples synthesized at  $800^\circ C$  under oxygen atmosphere. The diffraction peaks of all the samples corresponded to a single-phase spinel structure with  $Fd3m$  space group. Doping did not appear to change the host structure of  $LiMn_2O_4$ , but slightly changed the lattice parameters due to the various ion radii of the dopants. The calculated lattice parameters of the prepared samples were shown in Fig. 4. As can be seen Fig. 4, the

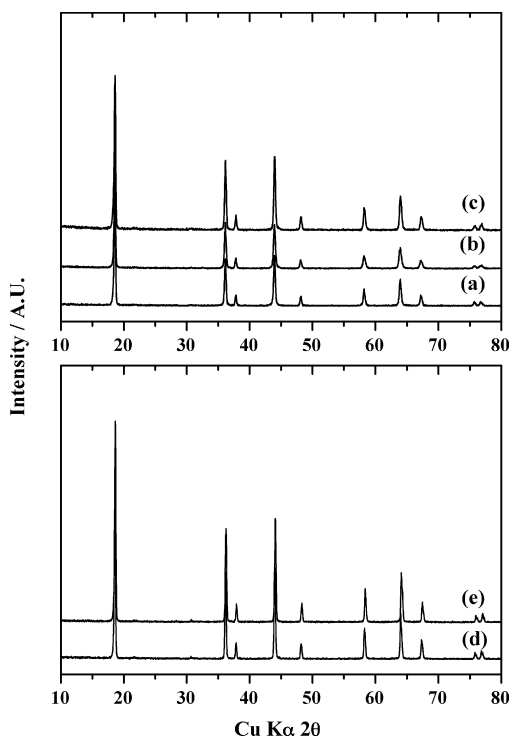


Fig. 3. XRD patterns of  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$ : (a)  $x=0$ ,  $y=0$  ( $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ ); (b)  $\text{M}=\text{Mg}$ ,  $x=0.05$ ,  $y=0$ ; (c)  $\text{M}=\text{Al}$ ,  $x=0.05$ ,  $y=0$ ; (d)  $\text{M}=\text{Mg}$ ,  $x=0.1$ ,  $y=0.05$ ; (e)  $\text{M}=\text{Al}$ ,  $x=0.1$ ,  $y=0.05$ .

calculated unit cell volume of the  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  was  $550 \text{ \AA}^3$  of which agrees with the reported values [14].

On the other hand, all doped samples [ $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M}=\text{Mg}$  and  $\text{Al}$ ;  $x=0$ ,  $0.05$  and  $0.1$ ;  $y=0$  and  $0.05$ )] showed slightly decreased lattice parameters. As mentioned above, the variation of lattice parameters for all the doped spinel may be due to the differences of ion radii of dopants

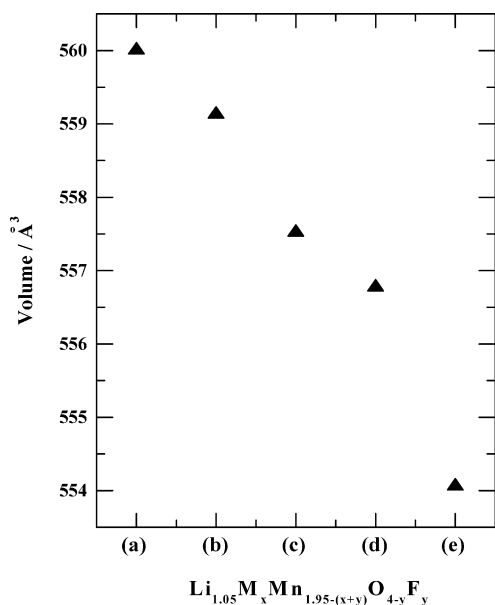


Fig. 4. Variation in unit cell volume of  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M}=\text{Mg}$  and  $\text{Al}$ ): (a)  $x=0$ ,  $y=0$  ( $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ ); (b)  $\text{M}=\text{Mg}$ ,  $x=0.05$ ,  $y=0$ ; (c)  $\text{M}=\text{Al}$ ,  $x=0.05$ ,  $y=0$ ; (d)  $\text{M}=\text{Mg}$ ,  $x=0.1$ ,  $y=0.05$ ; (e)  $\text{M}=\text{Al}$ ,  $x=0.1$ ,  $y=0.05$ .

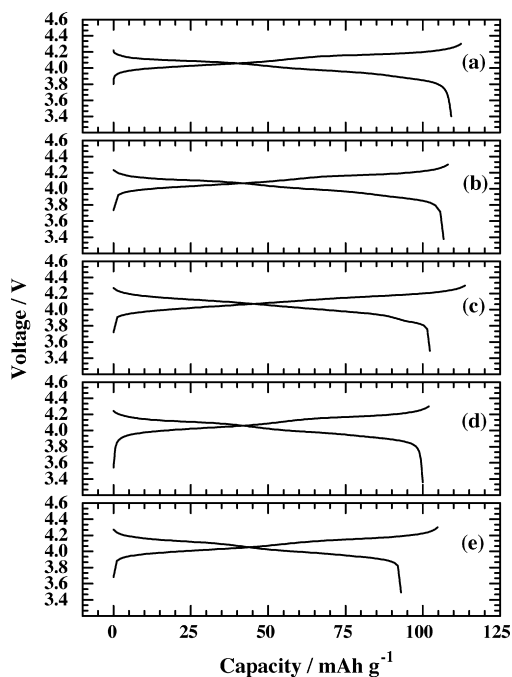


Fig. 5. Voltage profiles of  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M}=\text{Mg}$  and  $\text{Al}$ ): (a)  $x=0$ ,  $y=0$  ( $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ ); (b)  $\text{M}=\text{Al}$ ,  $x=0.05$ ,  $y=0$ ; (c)  $\text{M}=\text{Al}$ ,  $x=0.1$ ,  $y=0.05$ ; (d)  $\text{M}=\text{Mg}$ ,  $x=0.05$ ,  $y=0$ ; (e)  $\text{M}=\text{Mg}$ ,  $x=0.1$ ,  $y=0.05$  at a current level of  $0.4 \text{ mA cm}^{-2}$  at  $55^\circ\text{C}$ .

( $\text{Al}=0.535 \text{ \AA}$  and  $\text{Mg}=0.69 \text{ \AA}$ ). Furthermore, change of lattice parameter can be used to estimate the ratio between  $\text{Mn}^{3+}/\text{Mn}^{4+}$  since ionic radii of  $\text{Mn}^{3+}$  (HS, high spin state) is larger than that of  $\text{Mn}^{4+}$  [15]. It is worthy to notice that F-doped spinel with larger amount cation doping ( $x=0.1$ ) also showed decreased lattice parameters. Monovalent element such as fluorine substitution for oxygen can increase the  $\text{Mn}^{3+}$  contents which may result in the opposite effect on the lattice parameters [15].

Fig. 5 shows the comparison of charge and discharge behaviors for  $\text{Li}/\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M}=\text{Al}$  and  $\text{Mg}$ ;  $x=0$ ,  $0.05$  and  $0.1$ ;  $y=0$  and  $0.05$ ) coin cells at constant current of  $0.4 \text{ mA cm}^{-2}$  at  $55^\circ\text{C}$  over the voltage range of  $3.4\text{--}4.3 \text{ V}$ . The  $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  was also included in the study for comparison of the cells having the prepared substituted spinels.

The  $\text{Li}/\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  shows about  $110 \text{ mAh g}^{-1}$  corresponding to  $0.7\text{--}0.75$  of total lithium in  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  reversibly utilized within the voltage range of  $3.4\text{--}4.3 \text{ V}$ . Compared to the  $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ , Al-doped spinel ( $\text{Li}_{1.05}\text{Al}_{0.05}\text{Mn}_{1.9}\text{O}_4$ ) exhibited the slightly decreased capacity of  $107 \text{ mAh g}^{-1}$ . The discharge capacity for Mg doped was also decreased to  $100 \text{ mAh g}^{-1}$ . Cationic (Mg and Al) substitution decreases the amount of  $\text{Mn}^{3+}$  in the  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  structure which is a reversible redox species in the test voltage range [14]. Consequently, the specific capacity of  $\text{Li}_{1.05}\text{M}_{0.05}\text{Mn}_{1.9}\text{O}_4$  ( $\text{M}=\text{Mg}$  and  $\text{Al}$ ) was expected to be reduced. The  $\text{Li}/\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  exhibited  $102 \text{ mAh g}^{-1}$  even though the amount of cationic substitution increased to  $0.1$ . Fluorine substitution may compensate the effect of cationic substitution on the ratio of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  which decreased the amount of  $\text{Mn}^{3+}$ . However, the capacity of

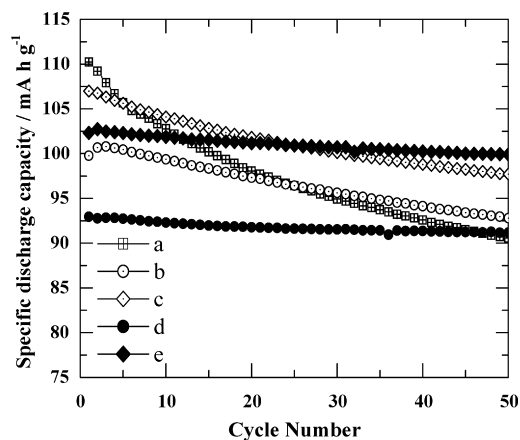


Fig. 6. Cycling performances of  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M} = \text{Mg}$  and  $\text{Al}$ ): (a)  $x=0, y=0$  ( $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ ); (b)  $\text{M} = \text{Mg}, x=0.05, y=0$ ; (c)  $\text{M} = \text{Al}, x=0.05, y=0$ ; (d)  $\text{M} = \text{Mg}, x=0.1, y=0.05$ ; (e)  $\text{M} = \text{Al}, x=0.1, y=0.05$  at a current level of  $0.4 \text{ mA cm}^{-2}$  in the voltage range of  $3.4\text{--}4.3 \text{ V}$  at  $55^\circ\text{C}$ .

$\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  cell was decreased, compared to the  $\text{Li}_{1.05}\text{Al}_{0.05}\text{Mn}_{1.9}\text{O}_4$ . The  $\text{Li}/\text{Li}_{1.05}\text{Mg}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  showed the lowest capacity of  $93 \text{ mAh g}^{-1}$ .

The effects of the cationic ( $\text{Mg}$  and  $\text{Al}$ ) and anionic ( $\text{F}$ ) substitution for spinel on the cycling performance at the elevated temperature ( $55^\circ\text{C}$ ) were evaluated in the voltage range of  $3.4\text{--}4.3 \text{ V}$  at a constant current of  $0.4 \text{ mA cm}^{-2}$ . All substituted spinel showed the improved cycling performance at the elevated temperature ( $55^\circ\text{C}$ ), compared to  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  (Fig. 6). Among them, the  $\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  exhibits better capacity retention (98% at 50th cycle) than the other substituted spinel. The initial capacity of  $\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  is  $102 \text{ mAh g}^{-1}$  which is lower than  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  and  $\text{Li}_{1.05}\text{Al}_{0.05}\text{Mn}_{1.9}\text{O}_4$ . However, based on the capacity retention, it can be inferred that  $\text{Al}$ - and  $\text{F}$ -substituted spinel merit long-term cycle life investigation at the elevated temperature as a promising candidate for lithium-ion batteries.  $\text{Li}_{1.05}\text{Mg}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  also showed good capacity retention but delivered relatively low capacity ( $93 \text{ mAh g}^{-1}$ ).

#### 4. Conclusions

Cation- and anion-doped spinel  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M} = \text{Al}$  and  $\text{Mg}; x=0, 0.05$  and  $0.1; y=0$  and  $0.05$ ) were synthe-

sized using metal oxide precursor by co-precipitation method. XRD revealed that the prepared  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M} = \text{Al}$  and  $\text{Mg}; x=0, 0.05$  and  $0.1; y=0$  and  $0.05$ ) has spinel structure with  $Fd3m$  space group. Well-crystallized  $\text{Li}_{1.05}\text{M}_x\text{Mn}_{1.95-(x+y)}\text{O}_{4-y}\text{F}_y$  ( $\text{M} = \text{Al}$  and  $\text{Mg}; x=0, 0.05$  and  $0.1; y=0$  and  $0.05$ ) showed improved cycling behavior at elevated temperature ( $55^\circ\text{C}$ ), compared to  $\text{Li}$ -excess  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ . Especially,  $\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  electrode exhibited an excellent cycle performance in the voltage range of  $3.4\text{--}4.3 \text{ V}$ . The capacity retention of  $\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_{3.95}\text{F}_{0.05}$  over 50 cycles was 98.1% while  $\text{Li}$ -excess  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  showed 82% capacity retention of the initial capacity.

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