Electrochemical Evaluation of Co-Al Dual-doped LiMn₂O₄ Spinels Synthesized Via Hydrothermal Method

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In order to improve the cycling performance of $LiMn_2O_4$ -based cathode materials, the Co-Al dualdoped $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ cathode materials were prepared by hydrothermal method followed by heat treatment. XRD patterns reveal that the dual-doped Al and Co in spinel lithium manganese oxide does not affect the Fd3m space group of the cathode materials. SEM shows that all $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ samples exhibit a uniform, nearly cubic structure morphology with narrow size distribution. The effect of the dual-doped Co-Al on the electrochemical performance of $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ was investigated by galvanostatic charge-discharge test, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results demonstrate that the synthesized Co-Al dual-doped LiMn₂O₄ materials gain better cycling stability and rate performance, which retains a capacity retention of 95.9% after 100 cycles at 1 C and deliver a higher capacity of 77.5 mAh·g⁻¹ at 8 C. This indicates superior cycling and rate performance compared with pristine one and single-phase doping of Al and Co.

Keywords: Lithium ion batteries; Co-Al dual-doping; Hydrothermal method; Spinel lithium manganese oxides

1. INTRODUCTION

Rechargeable lithium-ion battery is recognized as one of the most ideal electrochemical power supplies because of its safety, environmental protection, large capacity, long life, low consumption, and no memory effect, which is widely used in portable electronics devices, new energy vehicles, and energy storage systems [1]. Spinel lithium manganese oxide ($LiMn_2O_4$) is one of the most favored

cathode materials for lithium ion batteries because of the abundant manganese resources, low cost and environmental friendliness [2-3]. However, it is really a very unfortunate reality that the cycle performance of LiMn_2O_4 is not so excellent, which has been an obstacle to its wide spread application. So far, numerous studies have primarily linked the fast capacity fading with the following possible factors: dissolution of $\text{Mn}^{2+}[4]$, Jahn–Teller distortion of Mn^{3+} ions [5], oxygen deficiency[23], and the decomposition of electrolyte solution on the electrode [6].

To solve the problems mentioned above, most attention has been focused on the partial substitution of Mn or O, surface modification, and the control of particle size, structure and morphology. These methods have been proved to be effective in improving the electrochemical performance of materials, especially the method of doping [7]. Due to Mn^{3+} ion bears the major responsibility for the poor cycling performance of LiMn₂O₄ [8], doping by substituting electroinactive Mn with electroactive elements to increase the average valence state of Mn has been considered as an effective approach for the mitigation of structural distortion by the Jahn-Teller effect [9]. Therefore, $Li^{+}[10], Zn^{2+}[11], Ni^{2+}[12], Mg^{2+}[13], Al^{3+}[14], Cr^{3+}[15], Co^{3+}[16], Ga^{3+}[17], Ti^{4+}[18], and so on are$ considered to be the doped cations. Among these elements, Co doping is considered to be the most effective way. The substitution of Mn by Co is in favor for stabilizing the lattice structure of spinel LiMn₂O₄ and restrain the structural change of LiMn₂O₄ during cycling. It also enhances the rate performance due to larger Li-ion diffusion coefficient [19]. Furthermore, Al is also considered to be an ideal doping element for the properties of abundance, low cost and nontoxicity. Numerous related works indicated that the doping of Al and the excess of lithium can significantly improve the thermal stability of LiMn₂O₄ [20]. However, further study is needed for more details about the effect of dual doping of Co-Al on the structure and electrochemical performance of LiMn₂O₄.

In addition, the synthetic products by conventional solid-state reaction are usually irregular in surface morphology with a broad particle size distribution [21]. To overcome these disadvantages of the solid-state method produced, some soft-chemistry approaches such as sol-gel[22], Pechini[23] and co-precipitation[24] have been developed. However, the complicated production process and the high cost of raw materials have hindered the commercial use of LiMn₂O₄.

Herein, the $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (x=0.014, 0.028, 0.036, 0.042) spinels were synthesized via a hydrothermal process followed by a simple heat treatment approach using LiOH. H₂O and EMD as the raw materials. The aim of this work is to present the details of physicochemical and electrochemical properties of $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (x=0.014, 0.028, 0.036, 0.042). The results show that the dual doping of Co and Al ion can improve both the cycle performance and rate performance of the spinel materials and the $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ exhibits the optimal electrochemical performance.

2. EXPERIMENTAL

2.1. Synthesis procedure

 $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (x=0.014, 0.028, 0.036, 0.042) precursor was obtained by a hydrothermal process. The raw materials used were LiOH·H₂O (purity \geq 98.9%, Sichuan Tianqi Lithium Industries, Inc., China), C₄H₆O₄·Co·4H₂O (Purity \geq 99.5%, Sinopharm Chemical

Reagent Co., Ltd.), Al(OH)₃ (Purity \geq 99.5%, Tianjin Kermel Chemical Reagent Co., Ltd.) and electrolytic manganese dioxide (Mn \geq 59.36%, Xiangtan Chemical Industry). LiOH·H₂O, Al(OH)₃, C₄H₆O₄·Co·4H₂O and EMD in a stoichiometric ratio of Li:Al:Co:Mn=1.088:0.037:*x*:1.875-*x* was blended well and then put into a 1.0 L batch autoclave that has good sealing property (GCF-1 L, Weihai Jingda Chemical Machinery Co., Ltd.) with required deionized water. After kept 3 h at 150 °C, the autoclave was cooled down to 70 - 80 °C with the help of cooling water and then to separate the liquid and solid. Afterwards, the slurry was dried at about 110 °C in an oven, followed by a pre-heat treatment at 430 °C for 4 h and a calcination at 900 °C for 12 h in air atmosphere to obtain the final product.

2.2 Physical characterization

Powder X-ray diffraction (XRD) patterns were recorded using Rigaku D/max-2500 with Cu K α X-ray source in the 2 θ range of 10-80° at a scan rate of 8°/min.

The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JEOL JSM-6360LV) operated at 20 kV. Fourier transform infrared (FT-IR) spectroscopy was performed to study the structure co-ordination of as-synthesized powders with the Nicolet IS10 infrared spectrophotometer in the wavenumber range from 4000 to 400 cm⁻¹.

2.3 Electrochemical measurement

The electrochemical testing was performed with a 2016 coin type cells assembled in an Arfilled glow box (mBRAUN MB200G).

After mixing the active material (84 wt %) with acetyleneblack (8 wt %) and polyvinylidene fluoride (PVDF) binder (8 wt %) in an agate mortar, a certain amount of N-methylpyrrolidinone (NMP) were added as solvent, and a homogeneous slurry was obtained while grounding the mixture sufficiently. The slurry was coated on Al–foil and dried in a vacuum oven at 90 °C overnight. Then, it was cut into circular discs to use in the cell assembly, which is used as the cathode materials. The electrolyte was based on 1 M LiPF₆ in a 1:1(volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The assembled cells were charged and discharged at n C (**1** C=**148 mA·g**⁻¹) rate between 3.0-4.3 V at room temperature with Land (CT2001A) cell systems. Cyclic voltammogram (CV) was measured on an electrochemical workstation (VersaStat3, Princeton Applied Research) from 3.40 V to 4.30 V(vs. Li/Li+) with a scan rate of 0.1 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) was performed on the same workstation with the frequency range from 0.01 Hz to 100 KHz.

3. RESULTS AND DISCUSSION

3.1 Structure and morphology

The Rietveld refined X-ray diffraction patterns of the $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (x=0.014, 0.028, 0.036, 0.042) samples are shown in Fig.1(a). It can be seen that all the Al-Co doped materials show the similar diffraction peaks with $Li_{1.088}Mn_{1.912}O_4$. They

are both belong to single phase cubic spinel structure with space group Fd3m(JCPDS 35-0782), which indicates that the lithium ions occupy the tetrahedral 8a sites and transitional metal ions (Mn, Co and Al) reside at the octahedral 16d sites with O occupying 32e sites [25].



Figure 1. (a) XRD patterns and (b) lattice parameters of Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O₄ samples

Moreover, it is noticed that no traceable impurities such as manganese or aluminium, cobalt oxides are produced, suggesting the doped element embedded in the host structure. Comparing to Li⁺ radius (0.720 Å), the radius of Co³⁺ (0.545 Å) and Al³⁺ (0.54 Å) are closer to Mn³⁺ (0.645 Å) radius. Thereby, Co³⁺ and Al³⁺ may easily occupy the 16d positions and substitute manganese ions positions occupied in the crystal. As shown in Fig.1(a), the diffraction peak of (111) shift slightly but observably

towards large angle direction with the increase of cobalt doping content, further indicating that the cations are doped in the lattice. The modified compounds has a smaller lattice constants and cell volume, which is attributed to the smaller ionic radius of cobalt.

The effect of the cobalt content, incorporated into the lattice structure on the unit lattice parameter is shown in Fig. 1(b). Similar to reported by Wu et al. [26], the results indicated that lattice parameter decreases with the increasing of the content of cobalt linearly, which can be attributed to the smaller radius of AI^{3+} and Co^{3+} and the higher bond energy of Co-O (662 kJ·mol⁻¹) and Al-O (512 kJ·mol⁻¹). As a result, the decreases of lattice constant after dual doping modification may be conducive to improving the cycle performance. In addition, the decrease of lattice parameters results in larger specific surface area, which contributes to ensuring sufficient contact area between the active cathode and electrolyte, and then smaller concentration polarization at high rates [27].



Figure 2. The FTIR of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ samples

FT-IR spectra of the $Li_{1.088}Mn_{1.912}O_4$ and the $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ are presented in Figure.2. As can be seen, FTIR spectra of both the two samples are present in two spinel corresponding infrared absorption bands at 618 and 510 cm⁻¹. In addition, two absorption peaks of the $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ present slightly blue shift, which may be due to the greater Co-O bond energy (662 kJ ·mol⁻¹) and Al-O bond energy (512 kJ ·mol⁻¹) than the Mn-O bond energy (402 kJ ·mol⁻¹) [28]. On the other hand, the doping of Al-Co can enhance the interaction of Mn-O bond, which is conducive to inhibiting the Jahn-Teller distortion. This result is in good agreement with the smaller lattice parameter of $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ calculated from the XRD patterns. Both the

characteristic peaks of FTIR and XRD indicate the Al-Co dual-doped LiMn₂O₄ synthesized by hydrothermal method are spinel lithium manganese oxide.

Fig.3 shows SEM images of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (*x*=0.014, 0.028, 0.036, 0.042) particles. As can be seen, all samples are presented in the octahedral structure with smooth surface and clear edges, and show uniform particle distribution with their particle sizes ranging between 2 and 4 µm, which indicates good crystallinity of the materials. Notably, no significant changes are observed among the five samples, which demonstrate that minor doping of Co and Al ions has no effect on the morphology of pristine materials synthesized via hydrothermal method. The result may be due to the hydrothermal synthesis process, which is conducive to the mixing of Li, Mn ions and doping elements at atomic level.



Figure 3. The SEM images of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$

3.2 Electrochemical performances

The electrochemical performance of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (x=0.014, 0.028, 0.036, 0.042) are compared in Fig.4. Fig. 4(a) shows the initial charge and discharge curves of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ at 1C in the voltage range of 3.0–4.3 V at room

temperature. As can be seen, two well-defined plateau regions are observed for all compounds corresponding to the two-stage of Li de-insertion/insertion process in the crystal lattice, indicating that Al-Co dual-doping does not change the electrochemical characters regarding lithium ion occupation and deintercalation from the lattice of materials. It is obvious that the first discharge capacity decreases with the increasing of Co content, suggesting that reduction of the content of electrochemically active ingredients Mn^{3+} because of the substitution of Mn in the 16d site by Al and Co.



Figure 4. Electrochemical performance of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$, (a) discharge curves at 1C rate, (b) cycling performance at 1C rates, (c) discharge capacity retention, (d) rate capability.

It can be learned from Figure. 4(b) and Table 1 that the initial discharge capacity decreases with the increase of Co-doped content. However, the capacity retention of the materials after 100 cycles shows a tendency of increasing firstly and then decreasing. Capacity retention of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (*x*=0.014, 0.028, 0.036, 0.042) samples after 100 cycles were 92.6%, 94.5%, 95.9%, 93.9% and 89.4%, respectively, suggesting that appropriate doping of Co and Al improved cycle performance of materials at room temperature. However, as shown in Figure. 4(c), excessive doping leads to poor electrochemical performance due to excessive shrinkage of the unit cell volume of the material and local tension imbalance in the lattice, which give rise to the increasing of structural instability of materials. Therefore, the optimal Al-Co dual-doping spinel lithium manganate is $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ notably.

As is known, the rate performance, especially the high rate discharge performance, plays a crucial role in the application of cathodes for new energy vehicles power sources. The cycling performances of $\text{Li}_{1.088}\text{Mn}_{1.912}\text{O}_4$ and $\text{Li}_{1.088}\text{Al}_{0.037}\text{Co}_x\text{Mn}_{1.875-x}\text{O}_4$ samples at different rates are tested in the potential range between 3.0 V and 4.3 V in figure 4(d). Discharge capacity of un-doped samples at 1 C rate is 103 mAh·g⁻¹, while the rate increased to 2 C, 4 C and 8 C, the capacity gradually decreased to 96.9, 87.8 and 72.1 mAh·g⁻¹, respectively. As shown in Fig.4(c), the initial discharge capacity gradually decreases from 104.7 to 102.9, 101.1, 100.2 and 97.3 mAh·g⁻¹, as *x*=0, 0.014, 0.028, 0.036 and 0.042, respectively. However, the rate performance is improved after the Co-doping, especially when the content of cobalt is 0.028, its discharge capacity are 94.2%, 88.5% and 77.3% of 1 C at 2 C, 4 C and 8 C, respectively. Moreover, at high rate conditions of 8 C, rate performances of all cobalt-doped products are better than the un-doped one. The electrical properties of the samples doped with Co are significantly improved mainly because it improves the electrical conductivity and the diffusion coefficient of Li ions.

sample	Initial discharge capacity (mAh·g ⁻¹)	Discharge capacity after 100 cycle(mAh·g ⁻¹)	Capacity Retention
$Li_{1.088}Mn_{1.912}O_4$	104.7	96.8	92.6%
$Li_{1.088}Al_{0.037}Co_{0.014}Mn_{1.861}O_4$	102.9	97.3	94.5%
$Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$	101.7	97.5	95.9%
$Li_{1.088}Al_{0.037}Co_{0.036}Mn_{1.839}O_4$	98.6	92.6	93.9%
$Li_{1.088}Al_{0.037}Co_{0.042}Mn_{1.833}O_4$	97.6	87.3	89.4%

Table 1. Electrochemical result of Li_{1.088}Mn_{1.912}O₄ and Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O₄

Compared to the un-doped Li_{1.088}Mn_{1.912}O₄, Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O₄ with the optimal Al/Co -doped achieves significant improvement in the electrochemical performance, which delivers a discharge capacity of 78.6 mAh \cdot g⁻¹ at 8 C and retains 95.5% of its initial discharge capacity after 100 cycles. The results are superior to similar results reported by Chen et al. [29] and Pai et al. [30]. It is proved that the Co and Al doping enhances the stability of the spinel structure. On the one hand, Al and Co collaborative incorporation into the lattice and occupy 16d positions of Mn in the crystals, and the bond energy of Al-O (512 kJ·mol⁻¹) bond and the Co-O (662 kJ · mol⁻¹) bond are stronger than that of Mn-O (402 kJ · mol⁻¹) bond, all these make the lattice of materials more stable. In addition, the incorporation of elements of Al and Co substitution into the lattice will play a role of suppressing lattice contraction and expansion during the repeated reversible extraction and insertion process of Li⁺. As a result, it reduces the occurrence of Jahn-Teller effect at high temperature. On the other hand, due to the incorporation of Al and Co, the relative content of Mn³⁺ in the lattice is reduced, and the ratio of Mn³⁺ disproportionation reaction and inhibits the dissolution of manganese. Therefore, electrochemical

cycling performance of materials are significantly improved through doping of appropriate amount of Al and Co.





Figure 5. The first and the fifth cycle CV curves of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$

The first cyclic voltammetry curves of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ are shown in Figure.5 (a). The cells are cycled in the range of 3.4–4.3 V vs. Li/Li⁺/V and at a scan rate of 0.0001 Vs⁻¹ at room temperature. As can be seen from the figure, there are two pairs of reversible peaks, representing oxidation and reduction peaks present in the cyclic voltammetry of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ samples, which indicate that insertion and extrusion of Li^+ is a two-step reaction, corresponding to the two-phase transfer of $Li_{0.5}Mn_2O_4$ / $LiMn_2O_4$ and λ -MnO₂/Li_{0.5}Mn₂O₄[31]. It is clearly observed that $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ shows a better peak shape symmetry in the reduction and oxidation peaks, implying a better reversibility in the insertion and extraction process of lithium ions in the crystal lattice. Moreover, reduction peak potential rises while the oxidation peak potential decreases, suggesting that the charging platform reduces and discharging platform increases after modification.

The specific oxidation peak potential (φ_{pa}), the reduction peak potential (φ_{pc}), the redox potential difference $\Delta \varphi$ and the redox peak current ratio between the peaks *ipa / ipc* of both samples are

shown in Table 2. From the data in the table, it is evident that the potential difference $\Delta \varphi$ of Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O₄ sample between the reduction peaks and the oxidation peaks is smaller, which is corresponding to the current ratio 1.082 and 1.068, close to 1, indicating that Al-Co doped can enhance the intercalation/deintercalation reversibility of Li⁺. Therefore, electrochemical stability of the material in the cycle process is improved.

Sampla	Potential Values			Current		
Sample	$arphi_{ m pa}/({ m V})$	$\varphi_{\rm pc}/({ m V})$	$\Delta_{\varphi}(\mathrm{mV})$	$i_{\rm pa}/({\rm mA})$	$i_{\rm pc}/({\rm mA})$	$i_{ m pa}/i_{ m pc}$
$Li_{1.088}Mn_{1.912}O_4$	4.115	3.887	228	0.492	0.411	1.197
	4.215	4.067	148	0.551	0.422	1.306
$Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_{4}$	4.065	3.952	113	0.422	0.390	1.082
	4.186	4.085	101	0.452	0.423	1.068

Table 2. The CV peak potentials for $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$

The first and the fifth cycle cyclic voltammetry curves of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ are shown in Fig.5 (b) and Fig.5(c). As can be seen from the figures, the 1st and the 5th cycle cyclic voltammetry curves of $Li_{1.088}Mn_{1.912}O_4$ has shifted significantly and the reduction peak of the lower potential areas broadens, indicating that the material appeared great polarization during the cycle, while that of $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ is substantially coincident, indicating smaller electrode polarization in the charge-discharge process. This means after Al-Co doping, polarization of $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ in the cycle process is smaller and structural stability is enhanced. As a result, it leads to a better cycle performance, which is in good agreement with the results in Fig.5 (b) and Fig.5 (c).

3.4 Electrochemical impedance

To further understand the improvement of the high-rate capability of the Al/Co-doped samples, the electrochemical impedance spectra (EIS) of the $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ as electrodes were performed. Figure.6 shows the electrode AC impedance spectra of materials, wherein the dots represent the measured data and the line represents the fitting patterns. The fitting patterns shown in Figure. 6(a) are according to the equivalent circuitusing Zview software, and errors of all parameters are less than 8% during the fitting process. Fitting data obtained are shown in Table 3. Wherein, *Rs* is the ohmic resistance of electrolyte, *Rct* is the charge transfer resistance between the particles and the electrolyte, *CPE*1 represents the double electric layer capacitor, *Zw* is Warburg impedance, and *Z'* are the real and imaginary parts of the impedance unit. There is a semicircle in the high-frequency region and a slash in the low frequency parts in both figures. Among them, the size of the high frequency semicircle region is corresponding to the resistance (*Rct*) during the charge transfer process. When *Rct* value is smaller, the electrochemical reaction is carried out more easily, indicating better electrochemical performance. The slash in the low frequency region is corresponding

to the diffusion impedance of Li^+ in the solid phase. It is usually the diffusion rate that determines the electrochemical properties of materials, particularly rate performance.



Figure 6. (a) EIS of Li_{1.088}Mn_{1.912}O₄ and Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O₄ samples i (inset: equivalent circuit model for the electrode system). (b) Relationship between real impedance with the low frequencies of samples

Linear relationship between the impedance of the real parts Zre and the reciprocal of square root of the low frequency $\omega^{-0.5}$ is shown in Figure. 6(b), and the diffusion coefficient of Li⁺ calculated is shown in Table 3. As shown in figure. 6(b) and the data in table 3, the *Rct* value 221.8 Ω of Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O₄ reduces compared with the un-doped Li_{1.088}Mn_{1.912}O₄ (258.2 Ω) in the first cycle, while Rs of the samples is the same level. After 20 cycles, *Rs* and *Rct* of Li_{1.088}Mn_{1.912}O₄ sample increased significantly, as 22.46 Ω and 372.1 Ω , respectively, while *Rs* and *Rct* of Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O₄ samples increased in small range, as 4.743 Ω and 295.5 Ω , respectively. Along with the cycling, the charge transport resistance of electrode increases rapidly, showing that the charge transfer becomes difficult during the cycle due to the structure distortion of materials and the Jahn-Tettle effect.

Sample	cycl e	$R_{ m S}/\Omega$	Rct/Ω	CPE-T/F	W-T	$\sigma_{ m w}/\Omega m cm^2$ s ^{-0.5}	$D/\mathrm{cm}^2\mathrm{s}^{-1}$
	1^{st}	3.589	252.8	4.65E-5	0.033	69.8864	4.98×10 ⁻¹²
$L1_{1.088}Mn_{1.912}O_4$	20^{th}	22.46	372.1	4.84E-5	0.063	115.7624	1.96×10^{-12}
Li _{1.088} Al _{0.037} Co _{0.028} Mn	1^{st}	3.34	221.8	5.35E-5	0.033	40.6238	8.59×10 ⁻¹²
1.847O ₄	20^{th}	4.743	295.5	4.50E-5	0.001	43.5837	7.89×10^{-12}

Table 3. The impedance parameters of $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ samples

The charge transfer resistance of $Li_{1.088}Al_{0.037}Co_{0.028}Mn_{1.847}O_4$ electrode increases slowly, indicating that Al-Co doping effectively stabilizes the structure of material in the process of charging and discharging cycles. This means that a small amount of aluminum doping can improve conductivity and reduce polarization of the material. Diffusion rate of Li^+ in Co-doped samples calculated by the equation (2) after 20 cycles is approximately 7.89×10^{-12} , while that of the un-doped samples is approximately 1.96×10^{-12} . After the Al-Co binary complex doping, charge transfer rate and diffusion rate of lithium ion of the sample have been increased. As a result, the electrochemical performance including rate performance and cycle performance, achieves improvement, which is shown in Figure 4.

$$Z_{re} = R_{ct} + R_s + \sigma \omega^{-1/2} \quad (1)$$
$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{Li}^2 \sigma^2} \quad (2)$$

4. CONCLUSIONS

In this paper, single phase spinel $Li_{1.088}Mn_{1.912}O_4$ and $Li_{1.088}Al_{0.037}Co_xMn_{1.875-x}O_4$ (*x*=0.014, 0.028, 0.036, 0.042) materials are synthesized via a hydrothermal method followed by heat treatment, in which the value of *x*=0.028 is to be found the optimal doping amount of Co, which exhibited a higher capacity retention and better rate performance. XRD results show that Co-Al dual-doped lithium manganese oxide spinel remains Single phase spinel structure, and its lattice constant reduce linearly with the increasing of Co content, which is contributed to a more stable structure of the material. FTIR analysis show that all the peaks of the doped samples are fully consistent with the characteristic peaks of lithium manganese oxide spinel and M-O bond strength is enhanced after doping. CV characterization test results suggest that composite incorporation of Al-Co inhibits the redox peaks of high potential region corresponding to the electrochemical process, which means the doping of Al-Co greatly suppresses electrode polarization of lithium manganese oxide during charging and discharging process. The electrochemical impedance spectra confirms that Al-Co doped materials have smaller charge-transfer resistances and larger Li⁺ diffusion coefficients than the pristine sample during intercalation/de-intercalation process of Li⁺, which is contributed to significant improvement in the rate performance and cycle performance. These facts demonstrate that the improved

electrochemical property of spinel lithium manganate is due to the Al-Co substitution via hydrothermal method.

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