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Synthesis, characterization, and electrochemistry of cathode material Li [Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ using organic chelating agents for lithium-ion batteries

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HIGHLIGHTS

▶ We report a facile sol-gel method to synthesize Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂.

- Oxalic, tartaric and succinic acids are chosen as chelating agents.
- ► TA-material has the highest reversible capacity and the best rate performance.
- \blacktriangleright The reversible capacity is as high as 240.5 mAh g⁻¹ after 50 cycles at 0.1 C.
- ► The capacity fade mechanism has been preliminarily studied.

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ABSTRACT

Oxalic acid, tartaric acid (TA), and succinic acid (SA) are studied as chelating agents for sol–gel synthesis of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ as a cathode material for lithium-ion batteries. X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy show that the materials are single-phase compounds with good crystallinities and layered α -NaFeO₂ structures. The TA-material has the smallest particles (0.2–0.3 μ m), with a smooth surface, and uniform distribution. Electrochemical studies indicate that the TA-material exhibits the highest initial discharge capacity (281.1 mAh g⁻¹ at 0.1 C, 192.8 mAh g⁻¹ at 2.0 C), the highest reversible capacity after 50 cycles (240.5 mAh g⁻¹ at 0.1 C, 167.4 mAh g⁻¹ at 0.5 C), and the best rate performance. The cycling stability of the SA-material is the best, with capacity retentions of 87.4% at 0.1 C and 80.1% at 0.5 C after 50 cycles. Mn^{4+/3+} reduction peaks appear at the first discharge process and become more evident with increasing cycle number, resulting in a spinel structure, as proved by cyclic voltammetry and differential capacity curves. Electrical impedance spectroscopy confirms that the low charge-transfer resistance of the TA-material is responsible for its superior discharge capacity and rate performance.

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1. Introduction

Because of the limitations of nickel-metal-hydride batteries in terms of energy and power densities, lithium-ion secondary batteries, which have high energy densities, long cycling lives, and are lightweight, are expected to become energy sources for vehicle applications and consumer electronic devices such as cellular phones and laptops. Conventional cathode materials, such as layered LiCoO₂ and LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂, olivine LiFePO₄, and spinel LiMn₂O₄, cannot entirely meet the energy density demands. Manganese-based layered solid-solution cathode materials between layered Li₂MnO₃ and LiMO₂ (M = Mn, Co, Ni) have recently become the focus of studies as they can deliver much higher capacities (>250 mAh g⁻¹) at lower costs compared with commercial LiCoO₂ cathodes [1–6].

However, several major drawbacks of these attractive layered oxide cathodes have still to be overcome for their further use in practical application. One problem is the higher initial irreversible capacity loss (ICL) of 60–120 mAh g⁻¹, which can be effectively improved by surface modification with compounds such as AlPO₄, TiO₂, V₂O₅, Al₂O₃, CeO₂, ZrO₂, SiO₂, and ZnO [7–10]. The second



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shortcoming, their low rate capability, possibly resulting from the formation of a thick solid–electrolyte interfacial layer on the cathode surface during oxygen loss on charging to 4.8 V [11] or the low electronic conductivity induced by the insulating Li₂MnO₃ component [12], is significantly related to the preparation method. In addition, as a result of the deterioration of the electrode/electrolyte interface caused by side reactions with the electrolyte, the midpoint discharge voltages decrease during cycling, indicating increasing polarization of the electrode with increasing cycle number [13]. Another reason for the lowered midpoint voltage could be a layered-to-spinel transformation during initial activation of the Li₂MnO₃ component and the subsequent cycles [14].

Controlling the preparation conditions and modifying the synthesis method are effective and critical for overcoming these weaknesses and improving the electrochemical performances of lithium-rich cathode materials [15,16]. Coprecipitation is frequently used to prepare these materials [17–22]. However, there have been a few reports of sol-gel methods, using different organic acids as chelating agents, for the preparation of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ (0.5Li₂MnO₃·0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂), which has better electrochemical properties than other lithium-rich cathode materials [23]. In this work, three different organic acids, namely oxalic acid (OA), tartaric acid (TA), and succinic acid (SA), were used to assist the sol-gel synthesis of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂. The influences of the acids on the structures, morphologies, and electrochemical performances of $Li[Li_{0,2}Co_{0,13}Ni_{0,13}Mn_{0,54}]O_2$ cathode materials were investigated systematically. The analyses and comparisons clarified the characteristics and potential applications of the three different organic acid-assisted sol-gel methods.

2. Experimental

In this work, $\text{Li}[\text{Li}_{0.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ powders were synthesized by a sol-gel procedure using three different chelating agents, namely OA, TA, and SA. A 10% excess of lithium salt was used in the syntheses so that high yields with respect to the quantities of

transition-metal salts were obtained. All the chemicals used in this work were of analytical grade and not further purified.

Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ powder was prepared by a sol-gel method, using different organic acids as chelating agents, as follows (Fig. 1). Stoichiometric amounts of CH₃COOLi·2H₂O, Ni(CH₃COO)₂·4H₂O, Co(CH₃COO)₂·4H₂O, and Mn(CH₃COO)₂·4H₂O were dissolved together in distilled water. The mixed solution was added dropwise to an acidic solution of the chelating agent. The resulting solution was evaporated at 80 °C with continuous stirring until a transparent sol and then a gel were obtained. The dried precursor was precalcined in air at 450 °C for 5 h, ground uniformly, and made into pellets. The target compound was obtained by sintering the pellets at 900 °C for 16 h in air. The reaction scheme can be represented as follows:

$$\begin{split} & \mathsf{CH}_3\mathsf{COOLi} \cdot 2\mathsf{H}_2\mathsf{O} + \mathsf{Ni}(\mathsf{CH}_3\mathsf{COO})_2 \cdot 4\mathsf{H}_2\mathsf{O} + \mathsf{Co}(\mathsf{CH}_3\mathsf{COO})_2 \cdot 4\mathsf{H}_2\mathsf{O} \\ & + \mathsf{Mn}(\mathsf{CH}_3\mathsf{COO})_2 \cdot 4\mathsf{H}_2\mathsf{O} + \mathsf{C}_2\mathsf{H}_2\mathsf{O}_4 \\ & + \mathsf{O}_2 \! \rightarrow \! 0.5\mathsf{Li}_2\mathsf{MnO}_3 \cdot 0.5\mathsf{Li}\mathsf{Mn}_{1/3}\mathsf{Ni}_{1/3}\mathsf{Co}_{1/3}\mathsf{O}_2 + \mathsf{CO}_2 + \mathsf{H}_2\mathsf{O} \end{split}$$

$$\begin{split} & \mathsf{CH_3COOLi} \cdot 2H_2 \mathsf{O} + \mathsf{Ni}(\mathsf{CH_3COO})_2 \cdot 4H_2 \mathsf{O} + \mathsf{Co}(\mathsf{CH_3COO})_2 \cdot 4H_2 \mathsf{O} \\ & + \mathsf{Mn}(\mathsf{CH_3COO})_2 \cdot 4H_2 \mathsf{O} + \mathsf{C_4H_6O_6} \\ & + \mathsf{O_2} \to 0.5 Li_2 \mathsf{MnO_3} \cdot 0.5 Li \mathsf{Mn_{1/3}Ni_{1/3}Co_{1/3}O_2} + \mathsf{CO_2} + \mathsf{H_2O} \end{split}$$

$$\begin{split} & \mathsf{CH_3COOLi} \cdot 2H_2 \mathsf{O} + \mathsf{Ni}(\mathsf{CH_3COO})_2 \cdot 4H_2 \mathsf{O} + \mathsf{Co}(\mathsf{CH_3COO})_2 \cdot 4H_2 \mathsf{O} \\ & + \mathsf{Mn}(\mathsf{CH_3COO})_2 \cdot 4H_2 \mathsf{O} + \mathsf{C_4H_6O_4} \\ & + \mathsf{O_2} \to 0.5 Li_2 \mathsf{MnO_3} \cdot 0.5 Li \mathsf{Mn_{1/3}Ni_{1/3}Co_{1/3}O_2} + \mathsf{CO_2} + \mathsf{H_2O} \end{split}$$

All the samples were characterized using X-ray diffraction (XRD; Rigaku Ultima IV-185) with a Cu K α radiation source. Data was collected in the range 10–90° at a scan rate of 8° min⁻¹. Morphological studies and element distribution tests on the samples were



Fig. 1. Schematic illustration of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ preparation by sol-gel method using three different chelating agents.

performed using an FEI QUANTA 6000 scanning electron microscope (SEM) and an energy-dispersive X-ray (EDX) detector.

Electrochemical measurements were performed using galvanostatic cycling with two-electrode coin-cells (type CR2025). The electrodes were fabricated by coating a slurry of a mixture containing 80 wt% as-prepared active material. 10 wt% acetylene black. and 10 wt% polv(vinvlidene difluoride) on circular aluminum current-collector foils. The cells were assembled in an argon-filled glove box, using the prepared electrodes, metallic lithium foil as the counter electrode, 1 M LiPF₆ dissolved in ethyl carbonate and dimethyl carbonate (1:1 by volume) as the electrolyte, and a Cellgard 2400 membrane as the separator. Charge and discharge experiments were all performed under constant current conditions between 2.0 and 4.8 V at room temperature using Land battery testers (Land CT2001A, Wuhan, China). The assembled cells were measured for 50 cycles at current densities of 0.1C (20 mA g^{-1}) and 0.5 C (100 mA g^{-1}) to analyze the cycling performances of the materials. Various coulombic rates (0.1, 0.2, 0.5, 1.0, and 2.0 C) were tested to investigate the rate capability of the prepared materials. Cyclic voltammograms of the prepared materials were performed using a CHI electrochemical workstation (CHI660, Shanghai, China) at room temperature between 2.0 and 4.8 V at a sweep rate of 0.1 mV s^{-1} . Electrochemical impedance spectra (EIS) of the cells was also conducted using the CHI660 electrochemical workstation before charge and discharge at frequencies from 10⁵ Hz to 1 Hz with an AC perturbation signal of 5 mV. The EIS was analyzed using ZSimpWin software. The potentials throughout the paper are referenced to the Li/Li⁺ couple.

3. Results and discussion

3.1. XRD structural characterization

The XRD patterns of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ powders synthesized using three different organic acid-assisted (OA, TA, and SA) sol–gel methods are shown in Fig. 2a–c, respectively. No extra reflection peaks corresponding to any impurity phases are observed in the patterns, indicating the high purity of our prepared materials. Except for the superlattice peaks between 20° and 23°, all the peaks of the diffraction patterns can be indexed to the standard layered hexagonal α -NaFeO₂ structure with the space group R-3m. The low-intensity peaks between 20° and 23°



Fig. 2. XRD patterns of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ prepared by sol-gel method using three different chelating agents: (a) OA, (b) TA, and (c) SA.

(enlarged in the middle of Fig. 2), which can be indexed to the monoclinic unit cell C2/m [12,24], are characteristic of an Li_2MnO_3 -type structure with $LiMn_6$ (or Co- or Ni-substituted) cation arrangements in the transition-metal layers [12]. All lithium-rich layered oxides containing Mn possess this feature.

The layered oxide structure has lithium ions at the 3a sites, transition-metal ions (Ni, Co, Mn) at the 3b sites, and oxygen ions at the 6c sites. Since the ionic radii of Li⁺ (0.76 Å) and Ni²⁺ (0.69 Å) are similar, partial disordering among the 3a and 3b sites is expected, and is called "cation mixing". It has been established that cation mixing decreases the electrochemical performances of layered oxide materials. Morales et al. [25] reported that the (003) peak occurs as a result of diffraction of the layered rock-salt structure (R-3m), whereas the (104) peak appears as a result of diffractions of layered and cubic rock-salt structures. The integrated intensity ratio of the (003) to (104) lines (*R*) in the XRD patterns is regarded as a measurement of the cation mixing. Otherwise, the splitting of the lines assigned to the Miller indices (006, 102) and (108, 110) in the XRD patterns are characteristic of a layered structure [15].

The $I_{(003)}/I_{(104)}$ peak ratios of our three prepared samples are calculated to be 1.54, 1.49, and 1.41, respectively. Together with the clearly split (006)/(102) and (108)/(110) peaks, these indicate that all the powders have a pure phase with good crystallinity and a well-ordered layered structure.

3.2. SEM images and EDX spectroscopy

Differences among the morphologies and particle sizes of the three samples of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ cathode materials are evident, as shown in Fig. 3. The images show that all the powders consisted of well-crystallized relatively spherical particles with smooth surfaces and uniform distributions. There is little difference among the particle sizes of the materials prepared using the three different chelating agents, and the TA-material shows the smallest particle size (ca. $0.2-0.3 \mu m$) among the three. A small particle size in a cathode material is an important factor, as it gives a high surface area, and greatly influences the electrochemical properties such as rate capability and discharge capacity [26]. In general, a small particle size can accelerate lithium-ion reactions at the surface between the electrolyte and the electrode material and reduce the diffusion path of lithium ions inside the particle, meaning that lithium ions can be easily inserted into and extracted from their sites or into defects [27,28]. This is why our prepared TAmaterial delivers a high discharge capacity with good rate properties.

EDX spectroscopy was used to verify the distribution of 3d metals in the obtained materials. The EDX analysis results for Li [Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ are shown in Fig. 4 as a representative example because all three materials had the same composition. As can be seen in Fig. 4, all the materials are composed of Co, Ni, Mn, and O species; Li cannot be detected because of its low energy density. To identify the chemical compositions of the prepared samples, the molar ratio of each chemical species is calculated by dividing the number of moles of each species by the number of moles of Co. Fig. 5 shows a comparison of the theoretical stoichiometry values and the calculated molar ratios of Ni, Co, and Mn for the synthesized materials. Table 1 lists the calculated compositions for the three samples before and after the synthesis. It can be found that the molar ratios of the elements Ni, Co, and Mn were approximately the same as the theoretical values of 1:1:4, meaning that our synthesized samples were prepared with good stoichiometry. The distribution images of Co, Ni, and Mn (inserted in Fig. 4) show that the prepared materials were homogenous, which is consistent with the molar ratio values.



Fig. 3. Scanning electron micrographs of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ materials prepared by sol-gel method using three different chelating agents, at magnifications of \times 50k and \times 100k: (a and b) OA, (c and d) TA, and (e and f) SA.

3.3. Initial charge and discharge capabilities

The initial charge and discharge profiles, recorded from C-rates of 0.1-2.0 at room temperature, of $Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2$ synthesized using three different chelating agents are shown in Fig. 6. Under various constant current conditions, all the profiles show the same overall features. During the first charging process, the charge curves show turning points, distinguishing lithium extraction from LiMO₂- and Li₂MnO₃-like components, verifying that this type of lithium-rich electrode material consists of twocomponents [29]. The voltage plateaus before the point represent the formal oxidation processes of Ni²⁺ to Ni⁴⁺ and Co³⁺ to Co⁴⁺. The observed irreversible voltage plateaus after the point originate from an irreversible loss of oxygen from the lattice [30], resulting in activation of the oxidation states of Mn at the end of the first discharge. In addition, it can be seen that the TA-material has the



Fig. 4. EDX image of $Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2$ materials prepared by TA-assisted sol–gel method.

highest initial charge and discharge capacities at each rate, which may attribute to its shortest lithium-ion diffusion length because it has the smallest particle size.

The charge and discharge capacities, coulombic efficiencies, and ICLs of all the materials at the first cycle at various coulombic rates are listed in Table 2. The TA-material has a significantly higher initial discharge capacity of 281.1 mAh g⁻¹ at 0.1 C compared with those of the OA-material (269.0 mAh g⁻¹) and SA-material (250.6 mAh g⁻¹). The initial coulombic efficiencies at 0.1 C are all close to 70–80%, and the initial ICLs differ in the following order: SA (103.1 mAh g⁻¹) > OA (81.1 mAh g⁻¹) > TA (73.6 mAh g⁻¹). Among the three samples, the TA-material presents the lowest initial ICL, and the highest first discharge capacity and initial coulombic efficiency (79.25%) at 0.1 C. With increasing current density, the charge and discharge capacities and the coulombic efficiencies at the first



Fig. 5. Comparison of molar ratios of prepared Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2 measured by EDX, and theoretical values.

Table 1

Molar ratio data of prepared Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2 measured by EDX, and theoretical values.

Element	Molar ratio				
	Theoretical	OA	TA	SA	
Со	1	1	1	1	
Ni	1	0.976	0.962	1.031	
Mn	4	3.888	3.924	3.978	

cycle, for all three samples, decrease by different degrees, as shown in Fig. 7. The discharge capacity and coulombic efficiency of the TA-material are always the highest for rates of 0.1-2.0 C. At 2.0 C, the TA-material still has the highest charge and discharge capacities (276.5 mAh g⁻¹ and 192.8 mAh g⁻¹), the highest coulombic efficiency (69.73%), and the lowest ICL (83.7 mAh g⁻¹). Interestingly, the ICL of the SA-material from 0.1 C to 2.0 C decreases, unlike the cases of the OA-material and the TA-material.

3.4. Cycling performance

Fig. 8 compares the cyclical stability and capacity retention of the cells cycled at room temperature with two constant current densities of 20 mA g^{-1} and 100 mA g^{-1} . The cycling performances of all three materials at two different current densities show almost the same trends. This indicates that all the tested materials show a gradual decrease in discharge capacity, to different degrees, during the initial cycles. Interestingly, although the TA-material has the highest reversible discharge capacity among the three tested materials, its capacity retention is almost the lowest after 50 cycles (85.6% at 0.1 C, 69.9% at 0.5 C). Although the SA-material shows the lowest discharge capacity, the capacity fade at the tested current density is slower than that of the other two materials, with a capacity retention of 87.4% at 0.1 C and 80.1% at 0.5 C after 50 cycles. In general, the retained discharge capacities after 50 cycles follow the same trend: TA (240.5 mAh g⁻¹ at 0.1 C, 167.4 mAh g⁻¹ at 0.5 C) > OA (230.3 mAh g⁻¹ at 0.1 C, 154.2 mAh g⁻¹ at 0.5 C) > SA (219 mAh g⁻¹ at 0.1 C, 145.1 mAh g⁻¹ at 0.5 C), which is the opposite order to that for capacity retention, i.e., compared with the other two materials, the TA-material shows a high capacity with relatively low capacity retention in the tested cut-off voltage window.

Fig. 9 displays the discharge capacity of the TA-material at several different cycles in order to determine the reasons for the capacity fading. The discharge capacities at 0.1 C for the 1st, 2nd,



Fig. 6. First charge/discharge curves at various C-rates of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ materials prepared using different chelating agents (a) OA, (b) TA, and (c) SA.

Table 2

Charge and discharge capacities, coulombic efficiencies, and irreversible capacity
losses of Li[Li _{0.2} Co _{0.13} Ni _{0.13} Mn _{0.54}]O ₂ materials prepared by sol-gel method using
three different chelating agents.

Rate	Methods	1st Charge (mAh g ⁻¹)	1st Discharge (mAh g ⁻¹)	1st Coulombic efficiency (%)	1st Irreversible capacity loss (mAh g ⁻¹)
0.1 C	OA	350.1	269.0	76.84	81.1
	TA	354.7	281.1	79.25	73.6
	SA	353.7	250.6	70.85	103.1
0.2 C	OA	331.8	242.4	73.06	89.4
	TA	339	263.5	77.73	75.5
	SA	315.9	228.4	72.3	87.5
0.5 C	OA	315.1	220.3	69.91	94.8
	TA	314.8	239.4	76.05	75.4
	SA	263.9	181.2	68.66	82.7
1.0 C	OA	287.5	188.4	65.53	99.1
	TA	287.2	203.6	70.89	83.6
	SA	226.8	137.1	60.45	89.7
2.0 C	OA	237.2	151.7	63.95	85.5
	TA	276.5	192.8	69.73	83.7
	SA	215.6	124.4	57.70	91.2

5th, 10th, 20th, 30th, and 50th cycles are 281.1, 269.3, 266.6, 253.3, 248.4, 241.8, and 240.5 mAh g^{-1} . As can be seen, the discharge capacity of the TA-material degrades mainly in the initial 10 cycles, and remains stable in the following cycles. The midpoint voltages also become lower with increasing numbers of cycles, as a result of increasing polarization.

In order to investigate the capacity fade mechanism of Li $[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2$ prepared by the TA-assisted sol-gel method, differential capacity vs. voltage plots of Li/TA-Li $[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2$ cells at various cycle numbers at 20 mA g⁻¹ (0.1 C) are shown in Fig. 10. After the initial electrochemical activation of the Li₂MnO₃ component above 4.4 V, a dominant reversible redox reaction slightly below 3 V (marked by "&") occurs and becomes apparent as the redox reaction peaks (3.4 V/3.9 V, marked by " \Box ") of the layered structure weaken gradually [14], meaning that the layered structure of the TA-material is transformed to a spinel component on cycling to yield an unexpected layered-spinel intergrowth structure.

3.5. Rate performance

The rate capability is another standard for measuring the performance of a lithium-ion battery. A high rate capability is more



Fig. 7. Initial discharge capacities and coulombic efficiencies at various C-rates of Li $[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2$ materials prepared by sol-gel method using different chelating agents.



Fig. 8. Cycling performance comparison charts of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ materials prepared by sol-gel method using three different chelating agents at (a) 0.1 C (20 mA g^{-1}) and (b) 0.5 C (100 mA g^{-1}).



Fig. 9. Charge/discharge profiles at 0.1 C of 1st, 2nd, 5th, 10th, 20th, 30th, and 50th cycles for Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O_2 material prepared by TA-assisted sol-gel method.



Fig. 10. Differential capacity vs. voltage of Li/TA-Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ cell cycled at 20 mA g^{-1} (0.1 C) in the voltage range 2–4.8 V.

important than other factors in meeting the needs of high-storage applications. With the aim of demonstrating the rate capabilities of the Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ materials prepared using three different organic acids as chelating agents, the cells were cycled at various rates from 0.1 C to 2.0 C, and the results are compared in Fig. 11. It can be seen that as the applied current density increases, all the samples show gradual decreases in the discharge capacity, to different degrees, which can be attributed to the increasing polarization of the electrodes at high current densities. The polarization increases with increasing current rate as a result of the reduced time for Li⁺ ion intercalation into the crystal lattice, as only the surfaces of the active materials participate in the reaction [31]. Among the tested materials, the TA-material shows a relatively moderate capacity fade and delivers the highest discharge capacity at each current density. The average discharge capacity at 2.0 C (400 mA g^{-1}) of the TA-material is still 165.7 mAh g⁻¹. After 2.0 C, the discharge capacity of the TA-material at 0.1C can again reach 244.7 mAh g^{-1} , about 87.1% of the discharge capacity obtained in the first cycle. In general, the rate capability reduces in the following order: TA > OA > SA.



Fig. 11. Rate capabilities of Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ materials prepared by sol-gel method using three different chelating agents (a) OA, (b) TA, and (c) SA (0.1 C for five cycles, 0.2 C for five cycles, 0.5 C for five cycles, 1 C for five cycles, 2 C for five cycles, and 0.1 C for five cycles).

3.6. Cyclic voltammograms

Cyclic voltammetry (CV) was conducted for Li[Li_{0.2}Co_{0.13}-Ni_{0.13}Mn_{0.54}]O₂ to evaluate the redox potential of the transitionmetal ions during cycling. Fig. 12 represents the CV traces (the first three cycles) of the three materials between 2 and 4.8 V at 0.1 mV s⁻¹, in which metallic lithium acts as the counter and reference electrodes. The overall features of the different materials are the same. The peaks in the CV curves correspond to the phase transitions that occur upon lithium insertion and extraction.

In these CVs, the first anodic peak at approximately 4.0 V of the first cycle is associated with Ni oxidation from Ni^{2+} to Ni^{4+} and Co oxidation from Co^{3+} to Co^{4+} , but Mn remains in the 4 + oxidation state at the first charge. The second anodic peak, at a higher potential (4.6-4.7 V) is associated predominantly with the irreversible electrochemical activation reaction that strips Li₂O from the Li₂MnO₃ component to form an electrochemically active MnO₂ component [32–34]. In the first discharge process, when lithium is inserted back into the structure of the electrode, the peak observed at 3.7 V corresponds to the reduction of Ni^{4+} to Ni^{2+} and Co^{4+} to Co^{3+} , whereas the reduction peak below 3.5 V is assigned to the reduction of Mn^{4+} to Mn^{3+} [35], originating from the electrons generated during charging up to 4.8 V in the first charging process. The absence of oxidation reaction peaks below 3.5 V in the first charge profile indicates that the Mn ions are electrochemically inactive, and this also partly proves that our materials are synthesized with Mn^{4+} . The Mn^{4+}/Mn^{3+} reduction peaks become more evident in the following two cycles, which is in good agreement with our former analysis (the structural transformation). It can be found from the second and the third CV curves that the oxidation peak positions at 4.0 V shift slightly towards the lower voltage region and the oxidation peak observed at 4.6-4.7 V in the first charge disappears. The second and third cycle profiles almost overlap, demonstrating the good reversibility of the prepared materials.

3.7. EIS

EIS was used to further understand the origins of the different electrochemical performances of the materials prepared using three different organic acids as chelating agents. In this work, EIS of all the materials, investigated on the electrodes before charge/ discharge, using open-circuit cell voltages (about 3.1 V), are shown in Fig. 13. As can be seen, all of the EIS consisted of a high-frequency



Fig. 12. Cyclic voltammograms of Li/Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ cells.



Fig. 13. AC impedance spectra of Li/Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ cells.

semicircle and a low-frequency slope, as in standard Nyquist plots. The semicircle in the high-frequency section contains the contribution of interfacial charge-transfer through the surface layer of particles [36]. The rising line in the low-frequency section is related to the Warburg impedance, which is associated with the solid-state diffusion of lithium ions into the positive electrode [37]. The intercept of the semicircle with the horizontal axis (Z') at the highest frequency refers to the uncompensated ohmic resistance (R_{Ω}) between the working electrode and the reference electrode, and the diameter of the semicircle represents the charge-transfer resistance (R_{ct}). All three materials show insignificant R_{Ω} values and different R_{ct} values, indicating that the ohmic polarization of the investigated materials is negligible. The R_{ct} data of the three materials is in the following order: SA (110.7 Ω) > OA (62.8 Ω) > TA (26.4 Ω). The lower surface charge-transfer resistance of the TAmaterial than that of the other two materials is the reason why it has the highest rate capability among the three materials.

4. Conclusion

Composite electrode powders, Li[Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂, were successfully synthesized via a facile sol-gel technique, using three different chelating agents, i.e., OA, TA, and SA. All the prepared powders showed the α-NaFeO₂ structure with the R-3m space group and the characteristic peaks of the Li₂MnO₃ phase. Relatively spherical morphologies with smooth surfaces and uniform distributions were also observed. Among the three different materials, the TA-material, which had the smallest particles, showed the highest initial discharge capacity, the highest initial coulombic efficiency, the lowest irreversible capacity, the highest reversible capacity, and the best rate capability. The initial discharge capacity of the SA-material was the lowest, but its cycling performance was the best, with the highest capacity retention of 87.4% at 0.1C and 80.1% at 0.5 C after 50 cycles. In addition, the $Mn^{3+\!/\!4+}$ redox couple appeared and became more evident with increasing numbers of cycles; this is responsible for the structural transformation from a layered to a spinel component.

In general, because of the high capacities of the TA-material and the OA-material at low rates and the high content of manganese, which is cheap, there are good future prospects for the use of Li [Li_{0.2}Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ in power batteries with low C-rates. The SA-material has a long life, which is a necessary condition, because of its good cycling capabilities. It is still necessary to control the

synthetic conditions carefully to prepare materials with appropriate particle sizes, and in future research modifications should be adopted to overcome the drawbacks of these materials.

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