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Effect of niobium doping on the microstructure and electrochemical properties of lithium-rich layered Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2 as cathode materials for lithium ion batteries

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The niobium-doped lithium-rich layered cathode materials, Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2 (x = 0, 0.02, 0.04, and 0.06), were prepared and the effects of Nb doping on the microstructure and electrochemical properties were investigated. Upon Nb doping, the layered α-NaFeO_2 structure is maintained but with an expanded interlayer spacing and the electrochemical properties are significantly enhanced. In particular, the sample with x = 0.04 delivers a large reversible discharge capacity of 254 mAh•g\(^{-1}\) at 0.1C rate with a high capacity retention rate of 92.3% after 100 cycles. Furthermore, it delivers 198 mAh•g\(^{-1}\) at 1C rate, much larger than that of the undoped sample (125 mAh•g\(^{-1}\)). Capacity differential results reveal that strong Nb–O bond can stabilize the material structure and thus lead to a stable cycling performance.

Electrochemical impedance spectroscopy (EIS) analysis shows that Nb doping can decrease the whole diffusion path in the lithium-rich layered cathode materials, resulting in the excellent rate capability.

1. Introduction

In the past decade, lithium-ion batteries have been developed steadily as the portable energy storage devices, due to their higher energy and power density per unit as compared with other rechargeable battery systems. With the rise of electric enterprises, such as the Tesla motor, etc., the searching for safe and economical cathode materials with elevated voltage, high capacity and good cycle performance has become one of the focuses in recent years. Among the reported cathode materials, the lithium-rich (Li-rich) solid solution cathode materials between layered Li[Li_{1/3}Mn_{2/3}]O_2 (commonly written as Li_2MnO_3) and LiMO_2 (M = Mn, Co, Ni)\(^{1-12}\) have become attractive in recent years as they deliver a high capacity of around 250 mAh•g\(^{-1}\). Meanwhile, they have the advantages of reduced cost and improved safety as compared to the conventional LiCoO_2 cathode.

Nevertheless, these Li-rich material has some disadvantages, such as the large-capacity loss during the initial charge/discharge cycle, poor rate capability and the continuous voltage fading.\(^{13,14}\) To solve these problems, various attempts has been made, e.g. surface modification with metal oxides,\(^{15-18}\) shortening the lithium-ion diffusion pathways by reducing the particle size,\(^{19,20}\) and substituting a small amount of doping ions at the transition metal sites.\(^{21-25}\) It has been widely reported that the doping of fixed-valence-state elements, such as Al\(^{3+}\), Cr\(^{3+}\), Co\(^{3+}\), Ru\(^{4+}\), and F\(^−\), etc., could substantially improve the electrochemical performance of the Li-rich layered cathode materials.

It is known that the poor rate capability of Li-rich cathode could be related to the inferior electronic conductivity of Li_2MnO_3 component.\(^{3}\) On the other hand, part of Li_2MnO_3 component could transform from the layered structure to the spinel-like structure at the end of the first discharge process.\(^{28}\) To overcome these drawbacks, element doping has been reported to be an effective way by improving their thermal and structural stability.\(^{29}\) Element doping could prevent these structure transformations and enhance the diffusivity of electrons and lithium ions in the cathode materials.

According to Lange's Handbook of Chemistry,\(^{30}\) the bond dissociation energy of Nb–O (ΔH(Nb–O)=753 kJ•mol\(^{-1}\)) is stronger than that of Mn–O (ΔH(Mn–O)=402 kJ•mol\(^{-1}\)), which could contribute to the stability of the bulk layered structure. Meanwhile, the doped Nb\(^{5+}\) ions are expected to expand the Li\(^{+}\) channel in the layered structure due to their larger radius (0.69 Å) as compared to Mn\(^{4+}\) ions (0.53 Å).\(^{31}\) As far as we know, however, there is lack of studies on the electrochemical performance of Li-rich cathode materials doped by niobium. Thus, niobium ion (Nb\(^{5+}\)) is selected as a dopant to substitute Mn\(^{4+}\) in the layered Li-rich materials, Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2 (x = 0, 0.25, 0.5).

In the present work, Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2 (x = 0, 0.02,
0.04, and 0.06) compounds were prepared by a solid-state reaction, and the effects of niobium doping on the microstructure, and electrochemical behaviour of the materials were investigated. The mechanisms for the improved cycling performance and rate capability were also discussed.

2. Experimental

2.1 Synthesis of Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2

Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2 (x = 0, 0.02, 0.04, and 0.06) materials were synthesized by a two-step process. Firstly, a carbonate precursor Ni_{0.2}Mn_{0.6−x}CO_3 was prepared by co-precipitation of 2 M aqueous solution of Ni and Mn sulphate (Ni:Mn = (0.2:0.6−x) with the 2 M solution of Na_2CO_3 at the temperature of 55 °C. The pH was adjusted to approximately 8.0 by ammonium hydroxide (NH_4OH) solution. The obtained Ni_{0.2}Mn_{0.6−x}CO_3 was washed with deionized water for several times and subsequently dried in a vacuum oven. Secondly, the carbonate Ni_{0.2}Mn_{0.6−x}CO_3 was completely mixed with Li_2CO_3 and Nb_2O_5 according to the stoichiometric ratio, and then annealed in air at 500 °C for 5 h to decompose the carbonate precursors. The as-prepared powders were pressed into pellets. Finally, these pellets were sintered at 850 °C for 12 h in air and ground into powders. In addition, a 3 wt.% excess of Li_2CO_3 was added to compensate for lithium loss during the high temperature calcination.

2.2 Microstructure characterization

The phase structures of the as-synthesized products were examined by powder X-ray diffraction (XRD) (Philips-X PERT PRO diffractometer) using Cu Kα radiation. The morphology of the as-synthesized products was examined by Field emission scanning electron microscopy (FE-SEM, SIRION 200). In addition, X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo-VG Scientific) was performed to compare the compositions and ionic environments of the undoped and doped samples using an Al monochromatic X-ray (hv =1486.6 eV) source.

2.3 Electrochemical measurements

The electrodes were fabricated from a mixture of active materials, super-P carbon black and polyvinylidene difluoride (PVDF) in the ratio of 85:10:5 (wt.%). The PVDF was dissolved in N-methylpyrrolo-lidinone (NMP), and then the active material and Super-P carbon black were added. After homogenization, the slurry was evacuated to remove residual air. The slurry was coated on a thin aluminium foil (20 µm thick) and dried in a vacuum oven. The electrode was pressed and punched into round disks with 15 mm in diameter. The thickness of the electrodes was about 40-80 µm (mass loading of the active material 2.2-4.5 mg/cm²). Standard 2032 coin cells were assembled in a dry Ar-filled glove box to test the electrochemical properties of the cathode materials. Lithium metal foils were used as the counter electrode, and 1.0 mol/L LiPF_6/EC:EMC:DEC = 1:1:1) as the electrolyte. After aging for 10 h to ensure thorough wetting of the electrolyte, the coin cell was charged and discharged at room temperature within the range of 4.8–2.0 V (vs. Li⁺/Li). The electrochemical impedance spectroscopy (EIS) of the coin cell was evaluated in the frequency range from 0.01 Hz to 100 kHz at Zahner Zennium electrochemistry workstation. The amplitude of the AC signal was 5 mV.

3. Results and discussion

3.1 Microstructure characterization

XRD patterns of Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2 (x = 0, 0.02, 0.04, and 0.06) are shown in Fig. 1. Diffraction pattern of the undoped sample can be identified as a layered α-FeO_2 structure with space group R 3 m. Meanwhile, the splitting of [(1 0 8), (1 1 0)] and [(0 0 6), (1 0 2)] peaks is observed without any impurity reflections, indicating the highly ordered layered structure. The weak superstructure reflections observed around 20–25° (2θ) are known as the characteristic of a Li_2MnO_2-type structure with LiMn_6 (or Ni-substituted) cation ordering in the transition metal layers. In the doped samples, the main patterns are also consistent with the undoped layered structure. However, some minor residual peaks (as marked by asterisks) appear with the increase of the doping amount. For instance, in the sample with x = 0.06, distinct peaks emerge, which can be indexed as Li_xNbO_2 phase (PDF#00-016-0459) and Nb_2O_5 phase (PDF#00-070-2679). These impurities should originate from excess doping of niobium.
samples show similar curve shapes with a characteristic plateau around 4.5 V during charging process. According to Johnson,\(^1\) the initial charge slope below 4.5 V corresponds to the Li\(^{4+}\) extraction from the LiMO\(_2\) structure. The plateau around 4.5 V represents the activation of the Li\(_2\)Mn\(_2\)O\(_4\)-type structure, which only exists in the initial cycle. During the first charge, lithium and oxygen are electrochemically extracted from the electrodes according to Eq. (1) and Eq. (2).

\[
\begin{align*}
0.5Li_2MnO_2 + 0.5LiMn_{0.5}Mn_{0.5}O_2 & \rightarrow 0.5Li_2MnO_2 + 0.5Mn_{0.5}Mn_{0.5}O_2 + 0.5Li^+ + 0.5e^- \\
\text{Voltage below 4.5 V} & \quad \text{(1)} \\
0.5Li_2MnO_2 + 0.5Mn_{0.5}Mn_{0.5}O_2 & \rightarrow 0.5Mn_{0.5}Mn_{0.5}O_2 + Li^+ + e^- + 0.25O_2 \\
\text{Voltage around 4.5 V} & \quad \text{(2)}
\end{align*}
\]

Armstrong et al.\(^1\) have demonstrated that the formed oxygen ion vacancies would be eliminated with cationic and anionic rearrangements at the end of the initial charge, resulting in oxygen loss and structural reorganization in the Li-rich layered cathode material Li\([Li_{1/3}Ni_{1/2}Nb_{1/6}]O_2\).

The capacities of the initial charge-discharge are summarized in Table 1. It can be seen that the initial charge capacity of Li\([Li_{1/3}Ni_{1/2}Nb_{1/6}]O_2\) is 364 mAh\(\cdot\)g\(^{-1}\), approaching their theoretical values of 378 mAh\(\cdot\)g\(^{-1}\).\(^9\) However, the initial discharge capacity increases with the increasing niobium doping (except for \(x=0.06\)). As illustrated in Table 1, the electrodes with \(x = 0, 0.02, 0.04, \) and \(0.06\) deliver discharge capacities of 220, 235, 254, and 231 mAh\(\cdot\)g\(^{-1}\), respectively.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial charge capacity (mAh(\cdot)g(^{-1}))</th>
<th>Initial discharge capacity (mAh(\cdot)g(^{-1}))</th>
<th>Columbic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x = 0)</td>
<td>364</td>
<td>221</td>
<td>143</td>
</tr>
<tr>
<td>(x = 0.02)</td>
<td>339</td>
<td>235</td>
<td>104</td>
</tr>
<tr>
<td>(x = 0.04)</td>
<td>330</td>
<td>254</td>
<td>82</td>
</tr>
<tr>
<td>(x = 0.06)</td>
<td>319</td>
<td>231</td>
<td>88</td>
</tr>
</tbody>
</table>

Furthermore, one can see clearly that there is a large difference between the charge/discharge profiles of undoped material and the Nb-doped materials (Fig. 4a). For the initial charge profiles of Li\([Li_{1/3}Ni_{1/2}Nb_{1/6}]O_2\) (\(x = 0.02, x = 0.04\) and \(x = 0.06\)), the slopes below 4.5 V shift towards the lower voltage profile (represented as arrow in Fig. 4a). It is generally accepted that the average oxidation state of Mn may remain close to Mn\(^{3+}\) throughout the first charging process in cathode material Li\([Li_{1/3}Ni_{1/2}Nb_{1/6}]O_2\) and the capacity of this sloping region (~125 mAh\(\cdot\)g\(^{-1}\)) could be attributed to the oxidation of Ni\(^{2+}\) to Ni\(^{3+}\).\(^27\) The higher capacity (~175 mAh\(\cdot\)g\(^{-1}\)) in the sloping region indicates that other charge compensation mechanisms need to be considered. This could be ascribed to the presence of Mn\(^{4+}\), which is supposed to compensate the positive charge of the compounds in consideration of the substitution of Mn\(^{4+}\) by Nb\(^{5+}\). Assuming that all the nickel ions are divalent as they are in
LiMn$_{3-x}$Ni$_x$O$_2$, the average manganese oxidation state varying with $x$ in Li[Li$_{0.5}$Ni$_1$$_{x}$Mn$_{0.5-x}$]O$_2$ compounds can be calculated as +3.97 ($x = 0.02$), +3.93 ($x = 0.04$), and +3.89 ($x = 0.06$).

Hence, it is reasonable to infer the existence of Mn$^{3+}$ in the compounds.

XPS were carried out to determine the possible oxidation states of transition metal ions in the undoped sample and the sample with $x = 0.04$, and the corresponding spectra of pristine electrodes and charged electrodes for Mn are presented in Figure. 5a-d.

When the electrodes is charged to 4.8 V, we can find that the major peaks of the Mn(2p3/2) for the undoped sample and the sample with $x = 0.04$ centre at 642.21 eV and 642.41 eV, respectively. Binding energies (Bes) for the Mn element are in good agreement with the values reported for similar oxide cathode materials. It can be inferred that the main oxidations state of Mn in electrodes charged to 4.8 V is $4+$. However, before charge, the deconvolution of the Mn(2p3/2) spectrum (Fig. 5c) of the doped sample gives two Bes for its best fit. Comparing our Bes with the values of previous report, we note that the average oxidation state of Mn changes and the oxidation state of Mn ions is between $+3$ and $+4$ in the doped sample. This would give access to more electrons before the system has to oxidize oxygen ion to extract lithium-ions.

Chih Chieh et al. found that the length of the plateau region corresponded to the amount of oxygen loss from the lattice. Some factors could influence the degree of oxygen loss from the lattice, such as the binding of oxygen to the metal ions, electronegativity of the dopant ions, and the covalency of the metal–oxygen bond. Therefore, the stronger Nb-O bond suppresses irreversible extraction of O$^-$ from Li$_3$MnO$_3$ component during the first cycle.

Fig. 5a-h shows the O 1s XPS spectra of the pristine electrode and the charged electrode for the undoped sample and the sample with $x = 0.04$, respectively. It is clear that all the asymmetric O 1s peaks are well fitted by two Gaussian-Lorentzian functions. The former broad peak at higher binding energy represent a layer of C-O type species on the surface, which could originate from the oxidation of C-contained compounds. The latter peak at lower binding energy stands for M-O (M=Ni, Mn, Nb) bonds in the compound, contributing to the lattice of oxygen in the lithium-rich layered oxide. It is clearly observed that there are more C-O bonds and less M-O bonds, when the electrodes are initially charged to 4.8V for both samples. However, the Nb-doped sample shows more M-O bonds than that of the undoped sample, which means thatNb-doping has effects on the lattice oxygen and the Nb-doped sample has kept more lattice oxygen after the first charge.

Especially, for the initial charge profile of Li[Li$_{0.5}$Ni$_1$$_{x}$Mn$_{0.5-x}$]O$_2$ (x = 0.06), the slope below 4.5 V shows small change as compared to the undoped sample and the plateau around 4.5 V also becomes shorter. Besides the suppression of oxygen loss, this phenomenon should be due to the fact that the formation of Li$_3$NbO$_4$ in the compounds absorbs some lithium-ions. In contrast, the initial discharge capacity of the cathodes increases after niobium doping, resulting in lower irreversible capacity loss and higher coulombic efficiency. In the high-voltage region (4.8–3.7 V), the doping of Nb$^{5+}$ stabilizes the layered structure, resulting in more electrochemically active Li$^+$ extraction/reinsertion from the electrodes. In the low-voltage region (3.4–2 V), the capacity can be assigned to the reduction of Mn$^{3+}$ to Mn$^{4+}$, as proposed by Yu et al. However, if excessive niobium exists in the layered structure, it will form more Li$_3$NbO$_4$/Nb$_2$O$_3$ and thus reduce the amount of the active material.

These results are consistent with the XRD analysis. Therefore, a small amount of Nb doping can play a positive role in the Li-rich cathode material.

In order to understand the difference of redox reaction potential in the initial cycle of all the samples, plots of dQ/dV corresponding to the 1st cycle are shown in Fig. 4b. The high oxidation peaks around 4.5 V corresponding to the plateau in Fig. 4a can be attributed to the electrochemical removals of lithium and oxygen from the electrode, which is responsible for the large irreversible capacity loss. The peak decreases with increasing amount of niobium, indicating that the electrochemical removal of oxygen is suppressed by niobium substitution. The two small oxidation peaks at ~3.8 V and ~4.05 V can be ascribed to the redox-reaction of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$, respectively. However, for the sample with $x = 0.02$ and 0.04, the peaks around 3.8 V show broader width and have some shifting. The possible reason could be that the redox processes of Mn$^{3+}$/Mn$^{4+}$ are coupled with that of Ni$^{2+}$/Ni$^{3+}$. During the discharge, there are two peaks around 3.8 V and 3.3 V in the profile, as shown in Fig. 4b. The peak of ~3.8 V arises from the reduction reaction of Ni$^{3+}$, and the peak of ~3.3 V is probably related to the reduction of Mn$^{4+}$ in the activated layered MnO$_3$ component. On the other
hand, the sample with x = 0.06 shows a weak peak at ~3.3 V, indicating that less Mn^{4+} is reduced during the initial discharge.

3.2.2 The effect of niobium doping on cycling performance.

The cycling performances of all samples are shown in Fig. 6. All the cells are tested under a constant charge/discharge current density of 0.1C between 2.0 and 4.8 V. The discharge capacity of Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2 electrode rises at first and then decreases later, exhibiting only 83.4% of capacity retention after 100 cycles. In contrast, the Nb-doped electrodes show great improvement in cycling performance. For example, the sample with x=0.04 presents a high-capacity retention of 92.3% after 100 cycles. Corresponding to the evolution of oxidation reaction between 3.0 and 3.4 V, which explains the increase in capacity during the first few cycles in the lithium-ion batteries. However, the capacity gradually decreases during the following cycles. One reason is lattice break-up and formation of porosity, which are clearly observed in the Li-rich cathode material after almost complete activation of Li_2MnO_3 component. In addition, the HF in the electrolyte accelerates Mn dissolution from the spinel phase.

In comparison, the charge/discharge voltage profiles for the Nb-doped electrodes exhibit much more stability during cycling, as presented in Fig. 7c. The corresponding dQ/dV plots in Fig. 7d show that the shoulders shrink after the substitution. During the cycling, the shoulders grow slowly. In other words, the redox peaks are well maintained during the lithium-ion intercalation/deintercalation in the Nb-doped electrodes. This phenomenon should be ascribed to that Nb doping in the layered material can prevent the phase transformation and stabilize the host structure of cathode materials during charge/discharge cycling.

3.2.3 The effect of niobium doping on rate capability.

One of the most crucial electrochemical characteristics of the lithium-ion battery required for electric vehicles and energy storage application is the rate capability. In order to investigate the effects of Nb doping on the rate capability, the Li[Li_{0.2}Ni_{0.2}Mn_{0.6−x}Nb_{x}]O_2 (x = 0, 0.02, 0.04, and 0.06) electrodes were charged to 4.8 V at a galvanostatic density of 20 mA g\(^{-1}\) (0.1C) and discharged to 2.0 V at various current densities, viz., 0.1, 0.2, 0.5, 1, 2, and 5C. The discharge plots at various rates are presented in Fig. 8. The undoped sample Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2 shows a considerable discharge capacity at 0.1C and 0.2C rate, but it displays serious capacity fading at high rates. For example, it shows a high capacity of 225 mA h g\(^{-1}\) at 0.1C rate, but only 125 mA h g\(^{-1}\) at 1C rate. In contrast, the samples with x = 0.02, 0.04 and 0.06 have higher capacities at the same high discharge-rates. The undoped sample only delivers 125 mA h g\(^{-1}\) at 1C rate while
After the electrochemical cycle, the Nyquist plots show one arc in the high frequency region and two arcs in the high-to-medium frequency region. One of the arcs observed in the cycled materials could come from a contribution of the Li counter electrodes, and other two arcs could result from an SEI (passive solid electrolyte interface) layer and a charge transfer. During the charge/discharge process, the degradation of electrode surface caused by the massive SEI film formation and the modification of surface structure associated with lattice rearrangement lead to the variation of charge transfer impedance and the SEI film impedance. Thus, these arcs related to the surface condition of lithium and cathode electrodes are different from that of a fresh cell, and become larger with increasing cycle number. But it is risky to assign particular arcs to certain physical phenomena when Li foil served as both counter and reference electrodes during the EIS measurements. Therefore, we cannot precisely fit the experimental data to a certain model. But the whole cell impedance is decreasing clearly on doping and this observation is consistent with the expectation from previous lattice analysis.

3.2.4 EIS measurement.
Generally, the rate capability is closely related to the charge transfer reaction and Li diffusivity in the electrodes, and the electrochemical impedance spectroscopy (EIS) measurement is an effective method to investigate the involved reaction mechanisms. Fig. 9a shows the EIS in the Nyquist plane for Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6-x}$Nb$_x$]O$_2$ (x = 0, 0.04) cells before electrochemical cycling. In the Nyquist plots, the arc always represents the process of migration of Li ions through the surface films or charge transfer between the active material and electrolyte. The slope in the low frequency region refers to lithium-ion diffusion in the bulk material. Before cycles, the whole cell impedance of doped material is smaller than that of the undoped material.

Fig. 9b shows the EIS of Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6-x}$Nb$_x$]O$_2$ (x = 0, 0.04) cells after cycling for 100 times at 0.1C constant current between 2.0 and 4.8 V. Since the measurements were performed using a two-electrode cell, the impedance from the Li anode cannot be ruled out. According to La Mantia et al., impedance of the Li metal becomes stochastic at current densities above 1 mA·cm$^{-2}$, due to the dendrite formation, and can bring contributions to the whole cell impedance measurement. However, the major contribution of the impedance should come from the cathode.

Fig. 9 (a) EIS curves of samples prior to electrochemical cycling and (b) EIS curves of Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6-x}$Nb$_x$]O$_2$ (x = 0 and x = 0.04) after 100 cycles, as well as (c) the equivalent circuit used to fit the measured spectra.

In the low frequency region, the variation of charge transfer impedance and the SEI film characteristics are high for the undoped sample. All these results show that 4% Nb doping is the optimum content for the high-rate capacity of the doped material (x = 0.04) is able to deliver a capacity of 106 mAh·g$^{-1}$ at the same rate. Even when the cells were discharged at a current density as high as 5C rate, the doped material (x = 0.04) can still deliver a capacity of 106 mAh·g$^{-1}$, almost twice times more than that of the undoped sample. All these results show that 4% Nb doping is the optimum content for the high-rate capacity of the doped material (x = 0.04) is able to deliver 198 mAh·g$^{-1}$ at the 5C rate. Li$^{+}$ions can expand the Li layers and thus block the lithium-ion diffusion channel. However, Nb$^{5+}$ provides higher binding energy to the oxygen sheets of the layered structure and stabilizes the layered structure during the delithiation. On the other hand, the large radius of Nb$^{5+}$ can expand the Li$^{+}$ channels and facilitate fast migration of Li$^{+}$ ions. These results are consistent with the expectation from previous lattice analysis.

The rate capability of all the samples: discharge capacities under rates of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C in sequence for each 5 cycles. Fig. 8 The rate capability of all the samples: discharge capacities under rates of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C in sequence for each 5 cycles.
volume of the compound, \( \Delta E/\Delta x \) is determined from the galvanostatic titration curve, \( \tau \) is the diffusion time, and \( L \) is the finite length of the diffusion process.\(^{50}\) \( \alpha \) can be determined by the slope of the \( Z_{\text{diff}} \) vs. \( \omega^{-1/2} \) plots. As shown in Fig. 10, the slope of the undoped sample is larger than that of the doped sample (\( \alpha = 0.4 \)). As \( \alpha \) is inversely proportional to \( D \), it can reflect the trend of change for \( D \). Therefore, the doped sample exhibits higher mobility of Li-ion diffusion in the solid phase than that of the undoped sample.

Anyway, the above results and discussions confirmed that the improvement of the Li\(^+\) ion diffusion in the solid phase and structure stability are responsible for the better rate capability of the doped materials.

### 4 Conclusions

The Li-rich layered cathode materials, Li\([\text{Li}_{0.2}\text{Ni}_{0.3}\text{Mn}_{0.6-x}\text{Nb}_x]O_2\) (\( x = 0, 0.02, 0.04, \) and 0.06) were successfully synthesized by co-precipitation and solid-state reaction methods. The effects of niobium doping on the microstructure and electrochemical properties were investigated. A suitable amount of Nb\(^{5+}\) substitution for Mn\(^{4+}\) in the cathode material Li\([\text{Li}_{0.2}\text{Ni}_{0.3}\text{Mn}_{0.6-x}\text{Nb}_x]O_2\) has great improvements in initial columbic efficiency, cycling ability and rate capability. Among those electrodes, 4\% is the optimum content of Nb doping for the Li-rich cathode material Li\([\text{Li}_{0.2}\text{Ni}_{0.3}\text{Mn}_{0.6-x}\text{Nb}_x]O_2\) which shows the best electrochemical performances. The differential capacity curve and the EIS spectra were discussed to illustrate the mechanism of the improvements. All the electrochemical property enhancement of the Nb-doped materials can be attributed to three reasons.

i. The strong Nb–O bond can decrease the oxygen loss and maintain more Li\(^+\) with electrochemically active, resulting in higher coulombic efficiency.

ii. The suppression of layered-to-spinel phase transformation by Nb\(^{5+}\) doping reduces the increase of charge transfer resistance and stabilizes the host layered structure during the electrochemical cycling, resulting in better cycling ability.

iii. The relatively large radius of Nb\(^{5+}\) can expand the Li\(^+\) channels to facilitate fast migration of Li\(^+\), resulting in superior rate capability.

This material may benefit the development of advanced lithium-ion batteries that meet the electric vehicle and the renewable energy storage requirements.

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### References

41 B. Qiu, J. Wang, Y. Xia, Z. Wei, S. Han, Z. Liu, ACS applied materials & interfaces, 6 (2014) 9185-9193.
48 F. La Mantia, C. D. Wessells, H. D. Deshazer, Y. Cui, Electrochemistry Communications, 31 (2013) 141-144.
Upon Nb doping, the electrochemical properties of the Li-rich cathode material are significantly enhanced.