Electrical impedance of lithium nickel cobalt oxides doped with aluminium

V. Sethuprakhash¹ and W. J. Basirun*²

Three types of lithium nickel cobalt oxides doped with aluminium have been synthesised by a solid state reaction at 800°C for 18 h. The compounds were analysed using X-ray diffraction and gave sharp and well defined peaks. Electrical impedance spectroscopy was performed on all three materials, and conductivity measurements gave negative activation energies, which increased with the aluminium content. The largest variation in conductivities with temperature was found with the material with the highest aluminium content. Conductivity decreased with the increase in aluminium for all temperatures.

Keywords: Lithium nickel cobalt oxides, Cathode materials, Electrical impedance spectroscopy

Introduction

Numerous studies were performed on lithium nickel oxide materials as a possible candidate in lithium batteries. Mixed lithium nickel cobalt oxide has become the subject of interest of a few Japanese lithium battery manufacturers such as Sumitomo Mining. The addition of aluminium has been shown to give thermal stabilisation and prevent material degradation during cycling.¹ There have been electrochemical and thermal studies performed on aluminium substituted lithium nickel oxide materials such as LiNi1_y(Al)2O2.²⁻⁴

The study of three compounds with the formula LiNi0.4Co0.4(Al)2O2 with x=0, 0.05 and 0.1, prepared by solid state reaction, gave 177 mA h g⁻¹ for LiNi0.4Co0.4Al0.2O2.⁵ Here, the investigation is continued on these materials using electrical impedance spectroscopy (EIS).

Experimental

A stoichiometric mixture of LiNO3, Ni(NO3)2, Co(NO3)3 and Al(NO3)3 was put into a porcelain crucible in the desired proportions and annealed in a furnace for 18 h at 800°C. The materials were cooled to room temperature and ground into finer particles using agate mortar. The materials were analysed by X-ray diffraction (XRD) using a Philips PW 1840 diffractometer instrument with 2θ in the range of 10°–180°. The cathode materials were prepared into a pellet to be used in the EIS studies. Impedance was measured using a Hioki instrument with a range of 50 Hz to 2 kHz.

¹Sultan Idris Educational University (UPSFI), Technical and Vocational Faculty, Tanjung Malim, Perak 35900, Malaysia
²Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia
*Corresponding author, email wjeffreyb@yahoo.com

Results and discussion

X-ray diffraction

The XRD diffractograms for LiNi0.4Co0.4Al0.2O2 are shown in Fig. 1, and both LiNi0.4Co0.33Al0.25O2 and LiNi0.4Co0.3Al0.25O2 also show the same diffraction peaks at 2θ angles except the intensity varies for each sample. The XRD of the LiNi0.4Co0.4Al0.25O2 material is similar with previous reports.⁶ The intensity ratio of I₁₀₀/I₃₃₂₀ should be >1 to enhance the material performance according to Ohzuku et al.⁷ The intensity ratios I₁₀₀/I₃₃₂₀ for all three materials are 0.74, 1.17 and 1.10 for LiNi0.4Co0.4Al0.25O2, LiNi0.4Co0.3Al0.25O2 and LiNi0.4Co0.5Al0.25O2 respectively. Nitta et al.⁸ proposed that the peak intensity ratio for 101 and 006 peaks should be around 2.5–2.9 for high discharge. The intensity ratios of the 101 and 006 peaks I₁₀₁/I₃₃₂₀ for all three materials range from 1.25–2.25, which suggest good discharge capacity for the three materials. Previous results also confirmed that the highest discharge capacity among the three materials was for LiNi0.4Co0.4Al0.25O2, which gave 117 mA h g⁻¹.⁹

Electrical impedance spectroscopy

Figure 2 shows the Nyquist plots for LiNi0.4Co0.4Al0.25O2, where both LiNi0.4Co0.35Al0.25O2 and LiNi0.4Co0.3Al0.25O2 also show the same trend, and the resistance of the material increases with increasing temperature. Figure 3 shows the Arrhenius plots for the three materials, which give negative activation energies. The activation energies calculated from the Arrhenius equation log k= log A−(E_A/2.303RT) gave −2.43, −2.57 and −4.29 kJ mol⁻¹ for LiNi0.4Co0.4Al0.25O2, LiNi0.4Co0.35Al0.25O2 and LiNi0.4Co0.3Al0.25O2 respectively.

Figure 4 shows the relation between log (conductivity) for all three samples with various temperatures. It can be seen that the largest variation occurred for the material with the highest content of aluminium, i.e. LiNi0.4Co0.3Al0.25O2. A similar trend for substituting transition metals like Ni and Co with Al and Mg was also observed in previous reports.⁹ Chen et al.⁷ suggested that the
substantial increase in impedance with the increase in temperature is due to the increase in resistance of the charge transfer process, which occurs across the LiNiCoO₂ cathode and electrolyte. They attributed the rise in the resistance of the charge transfer process with the existence of a surface layer; hence, the effect of particle size has some effect on the impedance of the cathode material. They suggested that using a larger particle size cathode material could suppress the impedance rise, but the influence of the particle size to the impedance is only a secondary effect.

Chen et al.⁹ had also performed 5%Al doping on LiCoNiO₂ and found that the impedance of the 5% doped Al had a $Z_R$ value of 5.5, whereas the undoped LiCoNiO₂ had a $Z_R$ value of ~17, where a small amount of Al doping decreased the impedance value at various temperatures. They mentioned that the small amounts of Al doping had suppressed the increase in the charge transfer impedance.

However, Al doping of $>$10% is undesirable. Madhavi et al.⁷ reported that the undoped LiNiCoO₂ and $>$10% doped Al showed more capacity loss compared to 5 and 10%Al doped LiNiCoO₂ after 100 cycles. Since the rise of impedance could also contribute to the capacity loss during cycling, the doping of $>$10%Al into LiNiCoO₂ must have increased the impedance of the cathode material in their work, which can be corroborated with the results of the present study.

Conclusions
Lithium nickel cobalt oxides doped with aluminium have been successfully synthesised using the solid state reaction method at 800°C and gave sharp peaks in the XRD. The EIS results gave lower conductivities for materials with increasing aluminium content. The materials with more aluminium content showed greater variation in conductivities with temperature. All the materials have negative activation energies, and the activation energies became larger with the increase in aluminium content.

References
Dear Author

During the preparation of your manuscript for publication, the questions listed below have arisen. Please attend to these matters and return this form with your proof. Many thanks for your assistance.

<table>
<thead>
<tr>
<th>Query Reference</th>
<th>Query</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Author: Please confirm the running head.</td>
<td>Confirmed</td>
</tr>
<tr>
<td>2</td>
<td>Author: Refs. 6 and 7 were interchanged so that reference citations are now in sequence.</td>
<td>Confirmed</td>
</tr>
<tr>
<td>3</td>
<td>Figure 1, 3, 4 are poor in quality, please supply a higher resolution version if possible.</td>
<td>Please provide us 3 more days for better quality figures. But we cannot guarantee that we can provide better quality figures.</td>
</tr>
</tbody>
</table>