PREPARATION AND CHARACTERIZATION OF LITHIUM-BASED SOLID STATE BATTERY MATERIALS

By

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Three different cathodes such as LiMn$_2$O$_4$, LiCoO$_2$ and Li$_2$Ni$_8$O$_{10}$ were synthesized by the sol-gel technique. The said materials at low temperature were achieved through the low temperature technique. The X-ray diffraction study of the compounds confirmed the formation of single-phase compound at higher calcination temperature. At low temperatures the X-ray diffractogram of the samples showed the presence of low intensity diffraction lines with weak impurities indicating the existence of crystallinity but these were not indexed to any kind of impurities of LiMn$_2$O$_4$, LiCoO$_2$ and Li$_2$Ni$_8$O$_{10}$. The formation temperatures of the compounds were analyzed using DTA. The DTA studies showed clearly the lowest formation temperature and this formation temperature depends upon the gelating agent used in the present study. The lowest formation temperatures recorded were 208 °C for LiMn$_2$O$_4$, 201 °C for LiCoO$_2$ and 214 °C for Li$_2$Ni$_8$O$_{10}$.
The thermogravimetric analysis showed that the compounds were stable up to 800 °C. The EDAX analysis was performed for the compounds to identify the purity of the compounds. The EDAX spectrum showed that there was no impurity present in the compounds. It ascertained the formation of single-phase compounds by XRD. Because of low atomic weight lithium could not be detected other than that the EDAX showed the presence of the respective atoms. The particle size distribution of the compounds showed that the particles were distributed in large volume. The particle diameter increased with the increase of calcination temperature. Grinding reduced the large volume distribution and the particle diameter. After grinding by mortar and pestle hand grinder, the particle size was reduced much and the distribution was narrowed down, thereby the surface area of the particle was increased.

The SEM analysis also confirmed the sub-micron size reduction and the distribution was narrowed down, thereby the surface area of the particle was increased. The compounds were used as electrode materials for lithium ion batteries. The battery analysis showed that the capacities of the LiMn$_2$O$_4$, LiCoO$_2$ and Li$_2$Ni$_8$O$_{10}$ were 10 mAh, 24 mAh and 5 mAh respectively.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN DAN PENCIRIAN BAHAN-BAHAN BATERI
KEADAN PEPEJAL LITIUM

Oleh

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Ogos 2000

Pengerurusi: Profesor Madya Mansor Hashim, Ph.D.

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Tiga jenis bahan katod iaitu LiMn$_2$O$_4$, LiCoO$_2$ dan Li$_2$Ni$_8$O$_{10}$ telah disintesis menggunakan kaedah itu ‘sol-gel’. Kaedah suhu rendah ini menghasilkan bahan-bahan yang tersebut di atas pada suhu rendah. Kajian belauan sinar-X terhadap sebatian-sebatian ini mengesahkan pembentukan sebatian fasa tunggal pada suhu ‘kalsinasi’ yang lebih tinggi. Pada suhu rendah difraktogram sinar-X sampel-sampel menunjukkan kewujudan puncak-puncak belauan yang kecil beserta kehadiran sedikit bendasing, menandakan kewujudan sifat kehabluran, tetapi tidak pula merujuk kepada sebarang ketidakutulenan LiMn$_2$O$_4$ teroksida. Suhu pembentukan sebatian tersebut dianalisa menggunakan kajian DTA menunjukkan dengan jelas suhu pembentukan terendah ini dan suhu pembentukan ini bergantung kepada ‘gelating agent’ yang digunakan didalam penyelidikan ini. Suhu pembentukan terendah yang direkodkan adalah 208°C bagi LiMn$_2$O$_4$, 201°C bagi LiCoO$_2$ dan 214°C bagi Li$_2$Ni$_8$O$_{10}$. 

SEM juga mengesahkan zarah-zarah tersebut adalah bersaiz sub-mikron. Sebatian-sebatian tersebut telah digunakan sebagai bahan katod bagi bateri litium-ion. Analisa ke atas bateri menunjukkan nilai kapasiti bagi LiMn$_2$O$_4$ adalah 10 mAh, bagi LiCoO$_2$ adalah 24 mAh dan bagi Li$_2$Ni$_8$O$_{10}$ adalah 5 mAh.
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"Verily never will Allah change the condition of peoples until they change it themselves (with their own souls)" - Al-Quran

Allah s.w.t blessed me throughout my life. The deepest glory and honor unto him. Without His help, I was unable to pursue and complete this impassable task of my doctoral research.

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Last, but not least, I wish to express my grateful heart to my children, wife, brothers, sisters, relatives and friends for their moral support, encouragement and love.
I certify that an Examination Committee met on 18th August 2000 to conduct the final examination of Muhammad Amin Idrees on his Doctor of Philosophy thesis entitled “Preparation and Characterization of Lithium-Based Solid State Battery Materials” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MUHAMMAD AMIN IDREES

Date: 11-09-2000
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52(a) First charge/discharge profile of a Li$_2$Ni$_8$O$_{10}$ cell

52(b) Second charge/discharge profile of a Li$_2$Ni$_8$O$_{10}$ cell

52(c) Third charge/discharge profile of a Li$_2$Ni$_8$O$_{10}$ cell

52(d) Forth charge/discharge profile of a Li$_2$Ni$_8$O$_{10}$ cell
<table>
<thead>
<tr>
<th>Symbol</th>
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<td>Ah</td>
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<tr>
<td>Ah/L</td>
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<td>Co(NO₃)₂ · 6H₂O</td>
<td>cobaltous(II) nitrate hexahydrate</td>
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<tr>
<td>C₆H₈O₇ · H₂O</td>
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<td>C₄H₆O₄</td>
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<td>DMC</td>
<td>dimethyl carbonate</td>
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E₀  standard potential (in volts)
EC  ethylene Carbonate
EPDM  ethylene propylene diene monomer
F  faraday constant (96,500 C or 26.8 Ah)
Fe  iron
g  gram
ΔG  Gibbs free energy change
I  current
IR  Internal resistance of a cell
Kg  kilogram
Li-ion  lithium-ion
LiNO₃  lithium nitrate
Li₂CO₃  lithium carbonate
Li₂Ni₈O₁₀  lithium nickel oxide
LiCoO₂  lithium cobalt oxide
LiMn₂O₄  lithium manganese oxide
LiClO₄  lithium perchlorate
LiMoS₂  lithium transition metal sulphide
LiMeSe₂  lithium transition metal selenide
LiMeO₂  lithium transition metal oxide
LiMoO₂  lithium metal oxide
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