


**AUTHOR QUERY FORM**

	<b>Journal:</b> EA	<b>Please e-mail or fax your responses and any corrections to:</b>
ELSEVIER	<b>Article Number:</b> 21583	<b>E-mail:</b> <a href="mailto:corrections.esch@elsevier.thomsondigital.com">corrections.esch@elsevier.thomsondigital.com</a>
		<b>Fax:</b> +353 6170 9272

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. Note: if you opt to annotate the file with software other than Adobe Reader then please also highlight the appropriate place in the PDF file. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult <http://www.elsevier.com/artworkinstructions>.

No queries have arisen during the processing of your article.

Thank you for your assistance.

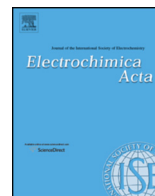
Please check this box or indicate your approval if  
you have no corrections to make to the PDF file



ELSEVIER

Contents lists available at ScienceDirect

Electrochimica Acta

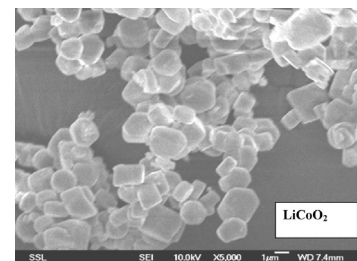
journal homepage: [www.elsevier.com/locate/electacta](http://www.elsevier.com/locate/electacta)

## Graphical Abstract

**Studies on Bare and Mg-doped  $\text{LiCoO}_2$  as a cathode material for Lithium ion Batteries**

M.V. Reddy\*, Thor Wei Jie, Charl J. Jafta, Kenneth I. Ozoemena,  
Mkhulu K. Mathe, A. Sree Kumaran Nair, Soo Soon Peng, M. Sobri Idris,  
Geetha Balakrishna, Fabian I. Ezema, B.V.R. Chowdari

Electrochimica Acta xxx (2013) xxx–xxx

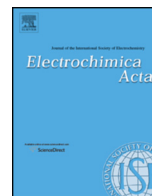




ELSEVIER

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: [www.elsevier.com/locate/electacta](http://www.elsevier.com/locate/electacta)

## Highlights

**Studies on Bare and Mg-doped LiCoO<sub>2</sub> as a cathode material for Lithium ion Batteries***Electrochimica Acta xxx (2013) xxx–xxx*

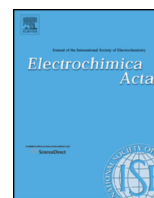
M.V. Reddy\*, Thor Wei Jie, Charl J. Jafta, Kenneth I. Ozoemena, Mkhulu K. Mathe, A. Sree Kumaran Nair, Soo Soon Peng, M. Sobri Idris, Geetha Balakrishna, Fabian I. Ezema, B.V.R. Chowdari

- Layered compounds, Li(Mg<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub> (x = 0, 0.03, 0.05) prepared by molten salt method.
- They were characterized by XRD, SEM, density and cyclic voltammetry and Galvano static cycling.
- Compounds showed reversible charge capacity values of 147 mAh/g (x = 0), 127 mAh/g (x = 0.03), and 132 mAh/g (x = 0.05), at the end of 60<sup>th</sup> cycle.



Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: [www.elsevier.com/locate/electacta](http://www.elsevier.com/locate/electacta)

## Studies on Bare and Mg-doped LiCoO<sub>2</sub> as a cathode material for Lithium ion Batteries

M.V. Reddy<sup>a,b,\*</sup>, Thor Wei Jie<sup>a,c</sup>, Charl J. Jafta<sup>d</sup>, Kenneth I. Ozoemena<sup>d,e</sup>, Mkhulu K. Mathe<sup>d</sup>, A. Sree Kumaran Nair<sup>f</sup>, Soo Soon Peng<sup>g</sup>, M. Sobri Idris<sup>g</sup>, Geetha Balakrishna<sup>h</sup>, Fabian I. Ezema<sup>i</sup>, B.V.R. Chowdari<sup>a</sup>

<sup>a</sup> Department of Physics, Solid State Ionics & Advanced batteries lab, National University of Singapore, Singapore 117542

<sup>b</sup> Department of Materials Science and Engineering, National University of Singapore, Singapore-1175763 Nanyang Junior College, 128 Serangoon Avenue 3, Singapore 556111

<sup>c</sup> Nanyang Junior College, 128 Serangoon Avenue 3, Singapore 556111

<sup>d</sup> Energy Materials, Materials Science & Manufacturing, Council for Scientific & Industrial Research, Pretoria 0001, South Africa

<sup>e</sup> Department of Chemistry, University of Pretoria, Pretoria, South Africa

<sup>f</sup> Amrita Centre for Nanosciences & Molecular Medicine, Amrita Institute of Medical Sciences, Amrita Vishwa Vidyapeetham, Kochi-682041, Kerala, India

<sup>g</sup> School of Materials Engineering, Universiti Malaysia Perlis, Malaysia

<sup>h</sup> Centre for Nano and Material Sciences, Jain University, Jakkasandra, Kanakapura, Bangalore rural-562112, India

<sup>i</sup> Department of Physics and Astronomy, University of Nigeria, Nsukka

### ARTICLE INFO

#### Article history:

Received 18 July 2013

Received in revised form 26 October 2013

Accepted 28 October 2013

Available online xxx

#### Keywords:

Molten salt method

Mg-doped LiCoO<sub>2</sub>

Cathode

Electrochemical properties

### ABSTRACT

In this paper, we report on the preparation of bare and Mg-doped Li(Mg<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub> (x = 0, 0.03, 0.05) phases by a molten salt method and their electrochemical properties. They were prepared at 800 °C for 6 h in air. Rietveld refined X-Ray Diffraction data of bare (x = 0) and Mg-doped (x = 0.03, 0.05) compounds show a well-ordered hexagonal layer-type structure (a ~ 2.81 Å, c ~ 14.05 Å). Scanning Electron Microscopy (SEM) show hexagonal type morphology at 800 °C. Powder density was close to 5.02 g cm<sup>-3</sup>, which compares well with the theoretical value. Electrochemical properties were studied in the voltage range of 2.5–4.3 V vs. Li using Cyclic Voltammetry (CV) and galvanostatic cycling. CV studies on bare and Mg-doped LiCoO<sub>2</sub> show main cathodic and anodic redox peaks at ~ 3.9 V and ~ 4.0 V, respectively. Galvanostatic cycling of Li(Mg<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub> (x = 0, 0.03, 0.05) showed reversible charge capacity values at the 60<sup>th</sup> cycle to be: 147 (±3) mAh g<sup>-1</sup> (x = 0), 127 (±3) mAh g<sup>-1</sup> (x = 0.03), and 131 (±3) mAh g<sup>-1</sup> (x = 0.05) cycled at a current density of 30 mA g<sup>-1</sup>. Capacity retention is also favourable at 98.5%.

© 2013 Published by Elsevier Ltd.

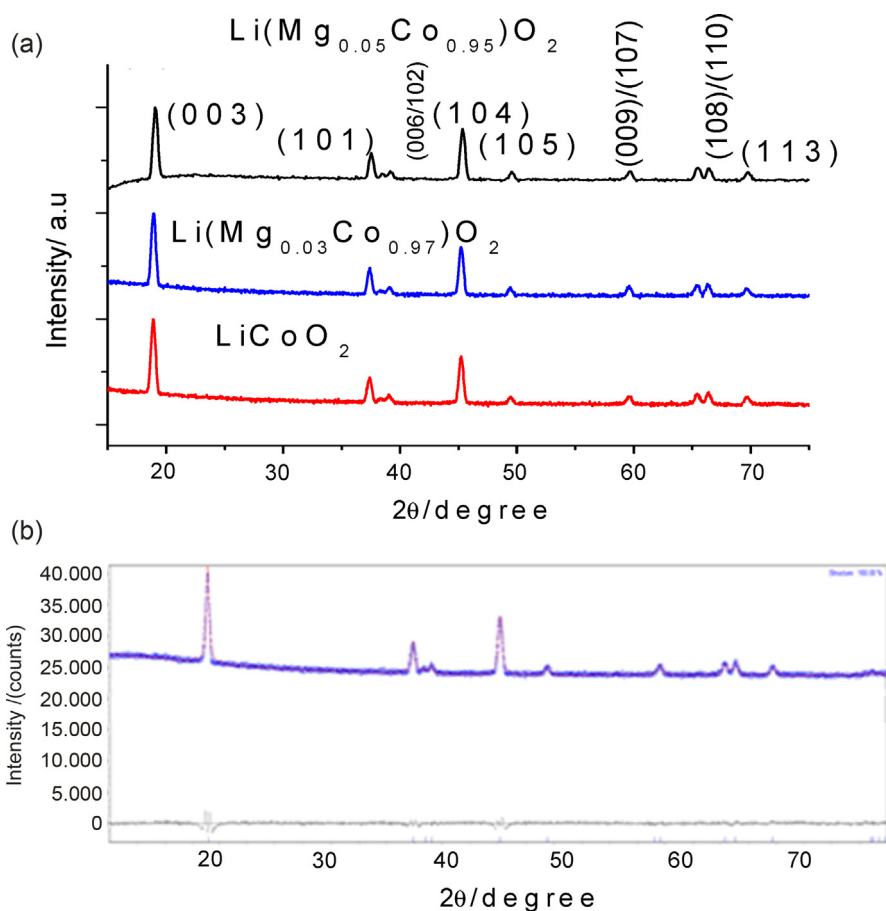
### 1. Introduction

Commercial Lithium ion batteries (LIBs) consist of a LiCoO<sub>2</sub>[1] or LiMn<sub>2</sub>O<sub>4</sub>[2,3] LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>[4,5] or LiFePO<sub>4</sub>[6] and other cathode as cathodes[7] and Graphite as anode[8,9]. During the charging process, Li-ions are removed from the cathode and inserted in the anode and vice-versa during the discharging process. The commercial cathode is usually lithium cobalt oxide (LiCoO<sub>2</sub>) due to its nice 4 V redox potential and its well-ordered layered structure while the anode is usually graphite due its flat discharge-charge potentials at 0.2–0.3 V[10]. LIBs are very successful due to their high energy density, low self-discharge and low maintenance, making them suitable for portable equipment from wireless communications to mobile computing.

Studies have shown that commercial batteries made of LiCoO<sub>2</sub> can deliver a reversible capacity of 120–140 mAhg<sup>-1</sup>. However, the capacities of the batteries fade when cycled at more than 4.2 V as it undergoes structural transformations due to various factors such as the preparation method, operating voltages and hexagonal structural transformations during cycling. The capacity fading can be reduced by suitable doping to the Co-sites, nanophase coating or novel preparation methods[11]. It was shown theoretically from first principles and determined experimentally that the substitution of Al increases the performance of the LiCoO<sub>2</sub> cathode[12]. However, it has been reported that Al doping causes capacity fading upon cycling[13]. Since Mg is a light element, cheap and abundant it is considered as a substituent (dopant) for Co, Mg is shown to stabilize the layered structure and therefore increase the cycle ability of the cathode material [14,15]. Previous studies also showed that the electronic conductivity of LiCoO<sub>2</sub> can be improved by Mg-doping[14,16–22]. In this project, Li(Mg<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub> (x = 0, x = 0.03, x = 0.05) compounds were prepared by the molten salt method (LiNO<sub>3</sub>:LiCl eutectic as the molten salt) at 800 °C, and their cathodic

\* Corresponding author.

E-mail address: [phymvvr@nus.edu.sg](mailto:phymvvr@nus.edu.sg) (M.V. Reddy).



**Figure 1.** (a) XRD patterns of  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x = 0, 0.03, 0.05$ ) of all samples, (b) Rietveld refined X-ray diffraction pattern of  $\text{LiCoO}_2$  synthesized using the molten salt method at  $800^\circ\text{C}$ . Vertical bars are Miller indices ( $hkl$ ) as shown and indexed.

performance was studied in a voltage range of 2.5–4.3 V at current rate of  $30 \text{ mA g}^{-1}$  for up to 60 charge-discharge cycles.

## 2. Experimental

$\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x = 0, 0.03, 0.05$ ) samples were prepared at  $800^\circ\text{C}$  by the molten salt method. The molten salt method is one of the simpler one-pot methods and usually its reactivity will be faster when compared to solid state reaction methods and this method offers defect free highly crystalline layered structure materials and no mixing and/or repeated reheating of the compounds are needed [23–27]. The initial reactants, 0.88 moles of  $\text{LiNO}_3$ , 0.12 moles of  $\text{LiCl}$ ,  $1-x$  moles of  $(\text{CH}_3\text{COO})_2\text{Co}$  and  $x$  moles of  $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were weighed and heated in an alumina crucible at  $800^\circ\text{C}$  in air for 6 h in a box furnace. After heating, the samples were cooled to room temperature before they were thoroughly washed with distilled water and filtered to remove the excess salts. They were then dried in an air oven at  $70^\circ\text{C}$  for 12 h. The black crystalline powder obtained was used for further studies. The material was characterized by X-Ray Diffraction (XRD) using the (Empyrean, Panalytical) to determine the structure of  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x = 0, 0.03, 0.05$ ). After XRD was performed, Rietveld Refinement was carried out using TOPAS-R software to compare the data obtained with literature. Scanning Electron Microscope (SEM) (model JEOL JSM-6700F) was also used to examine the morphology of  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x = 0, 0.03, 0.05$ ). The density and BET surface area of the powders were evaluated by Gas pycnometer and tristar (Micromeritics, USA). To fabricate the coin cells, a slurry had to be made. The slurry was made by mixing  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x = 0, 0.03, 0.05$ ), super

P carbon black and Polyvinylidene Fluoride (PVDF) in the weight ratio of 70:15:15, using N-Methyl-2-pyrrolidone (NMP) as a solvent, and it was stirred overnight before being spread on aluminum foil, which was the current collector. This was then dried at  $70^\circ\text{C}$  before it was cut into electrodes. The coin cells were then fabricated inside a glove box filled with argon gas, and each coin cell consisted of a bottom cap, the composite cathode on aluminum foil, an 1 M  $\text{LiPF}_6(\text{EC};\text{DEC})$  (Merck) as an electrolyte, a separator (Polypropylene-Cellguard), another few drops of electrolyte, Lithium foil and a top cap with O-ring and spring. It was then sealed with a press to form a coin cell of size 2016. After the coin cells were made in a glove box, electrochemical studies were performed using cyclic voltammetry (using Biologic, France) to determine the redox couple of the compounds. Galvanostatic cycling using Bitrode battery tester (USA) was done to evaluate the performance of the battery via. charge-discharge cycling at ambient temperature, with further details given in [28–30].

## 3. Results and discussion

### 3.1. Structure and morphology

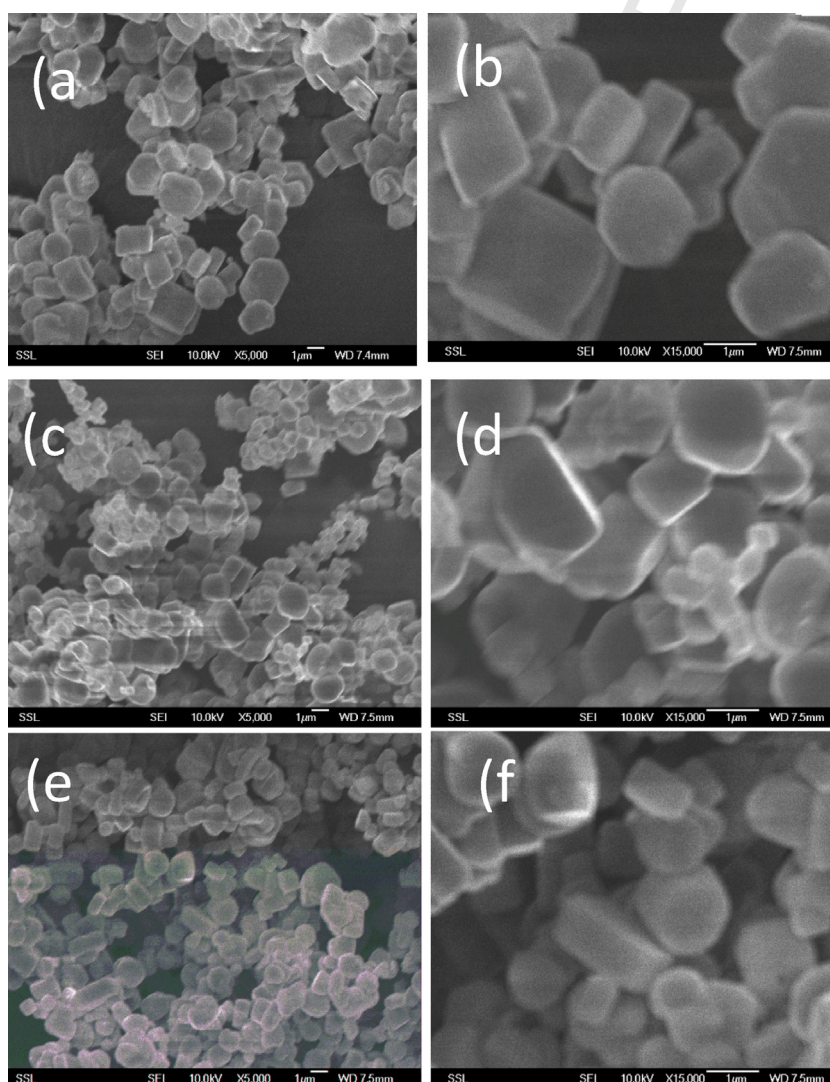
The XRD patterns of  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x = 0, 0.03, 0.05$ ) samples prepared at  $800^\circ\text{C}$  are shown in Figure 1a. The lattice parameters were refined using known space group (Fd-3m) and positional parameters [19]. For clarity, the refined XRD patterns of  $\text{LiCoO}_2$  are shown in Figure 1b. The obtained lattice parameters, Brunauer Emmett and Teller (BET) surface area values, as well as experimental and theoretical densities of all compounds are

**Table 1**The hexagonal lattice parameters,  $c$  and  $a$ , density and BET surface area, reversible capacity and % age capacity fading values.

Compound $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$	Lattice Parameter ( $\text{\AA}$ ) and cell volume ( $V$ )= ( $\text{\AA}^3$ )	Theoretical Density ( $\text{g}/\text{cm}^3$ )	Experimental Density ( $\text{g}/\text{cm}^3$ )	BET Surface Area ( $\text{m}^2\text{g}^{-1}$ )	Reversible capacity at 5 <sup>th</sup> and 60 <sup>th</sup> cycle ( $\text{mAhg}^{-1}$ ), Capacity fading (5–60cyc.) %
$\text{LiCoO}_2$	$a = 2.8153(4)$ $c = 14.0568(2)$ $c/a = 4.993$ $V = 96.489$	5.053	5.01	2.40	156; 147 (5.7)
$\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$	$a = 2.8162(2)$ $c = 14.0627(2)$ $c/a = 4.993$ $V = 96.589$	4.994	5.30	3.30	135; 127 (5.9)
$\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$	$a = 2.820(2)$ $c = 14.0936(7)$ $c/a = 4.997$ $V = 97.133$	4.931	4.94	3.43	136; 132 (2.9)

114 given in Table 1 Table 1. The XRD patterns of  $\text{Li}(\text{Co}_{1-x}\text{Mg}_x)\text{O}_2$  ( $x = 0,$   
115  $0.03, 0.05$ ) samples are similar to  $\text{NaFeO}_2$  and no impurity lines of  
116  $\text{Co}_3\text{O}_4$  or  $\text{MgO}$  lines were observed. The obtained lattice param-  
117 eter values are similar to reported literature on bare and doped  
118  $\text{LiCoO}_2$  by solid state method and other methods[14,18]. In brief  
119  $\text{LiCoO}_2$  showed a lattice parameter values  $a = 2.819(5) \text{\AA}$ ,  $c = 14.052$

(8)  $\text{\AA}$  [1,31], Lvasseur et al. reported a lattice parameter values of  
120  $a = 2.8212(1) \text{\AA}$ ,  $c = 14.082(1) \text{\AA}$  for  $\text{LiCo}_{0.94}\text{Mg}_{0.06}\text{O}_2$  [20]. When  
121 doping with  $\text{Mg}^{2+}$  the  $\text{Co}^{3+}$  ions are substituted and therefore there  
122 will be a charge compensation mechanism ( $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ ) taking  
123 place or oxygen vacancies will be created which leads to structural  
124 defect stabilizing  $\text{Co}^{3+(\text{IS})}$  ions. With the increase in  $\text{Co}^{4+}$  ions and  
125

**Figure 2.** Scanning Electron micrographs of (a,b)  $\text{LiCoO}_2$ , (c,d)  $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$ , (e,f)  $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$  with two different magnifications bar scale, 1  $\mu\text{m}$ .

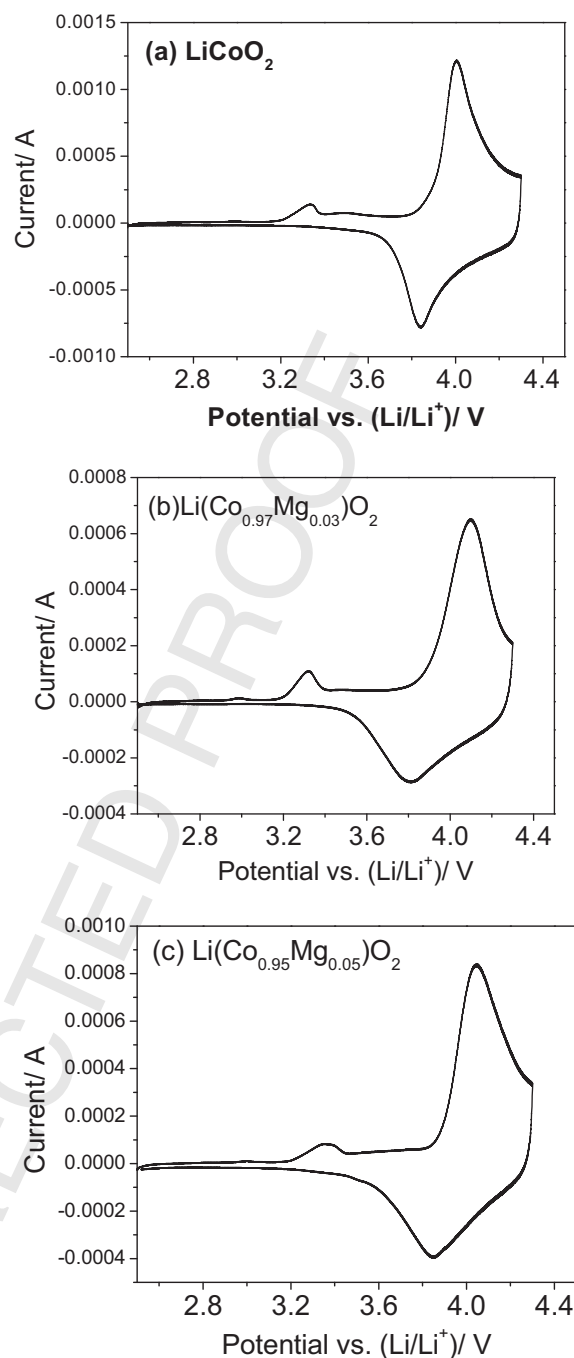
intermediated spin  $\text{Co}^{3+}$  ions, there will be an enhancement in the conductivity compared to the un-doped  $\text{LiCoO}_2$  [20]. Taking into account the ionic radii [32] of the  $\text{Mg}^{2+}$  (0.72 Å),  $\text{Co}^{3+}$  (0.545 Å) and  $\text{Co}^{4+}$  (0.53 Å) it is expected that there will be an increase in the lattice parameters with doping as seen in Table 1. Also when examining the  $c/a$  ratios it is worth noting that all samples have values greater than 4.90. This indicates a low degree of hexagonal phase distortion and a lack of cation disorder. The  $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$  shows the highest ratio of 5.00 making it structurally superior compared to the  $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$  and the  $\text{LiCoO}_2$  cathode materials and thus a better cyclability is expected.

SEM images of  $\text{Li}(\text{Co}_{1-x}\text{Mg}_x)\text{O}_2$  ( $x=0, x=0.03, x=0.05$ ) with different magnifications are shown in Figure 2(a-f) Figure 2, those of  $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$  at different magnifications are shown in Figure 2c,d, while the results for  $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$  prepared at different magnifications are shown in Figure 2e,f. The SEM images showed that the particles have a hexagonal shape, are of sub-micron size and that there are not many differences in the morphology of the doped samples. The formation mechanisms are very complex as they depend on temperature and nature of the molten salt and metal ions. Further careful studies on the effect of different Co-salts, preparation temperature are in progress. The BET surface area are in the range, 2–4  $\text{m}^2\text{g}^{-1}$  (Table 1). The experimental density values are similar to the theoretical density values calculated from the XRD data.

### 3.2. Electrochemical studies

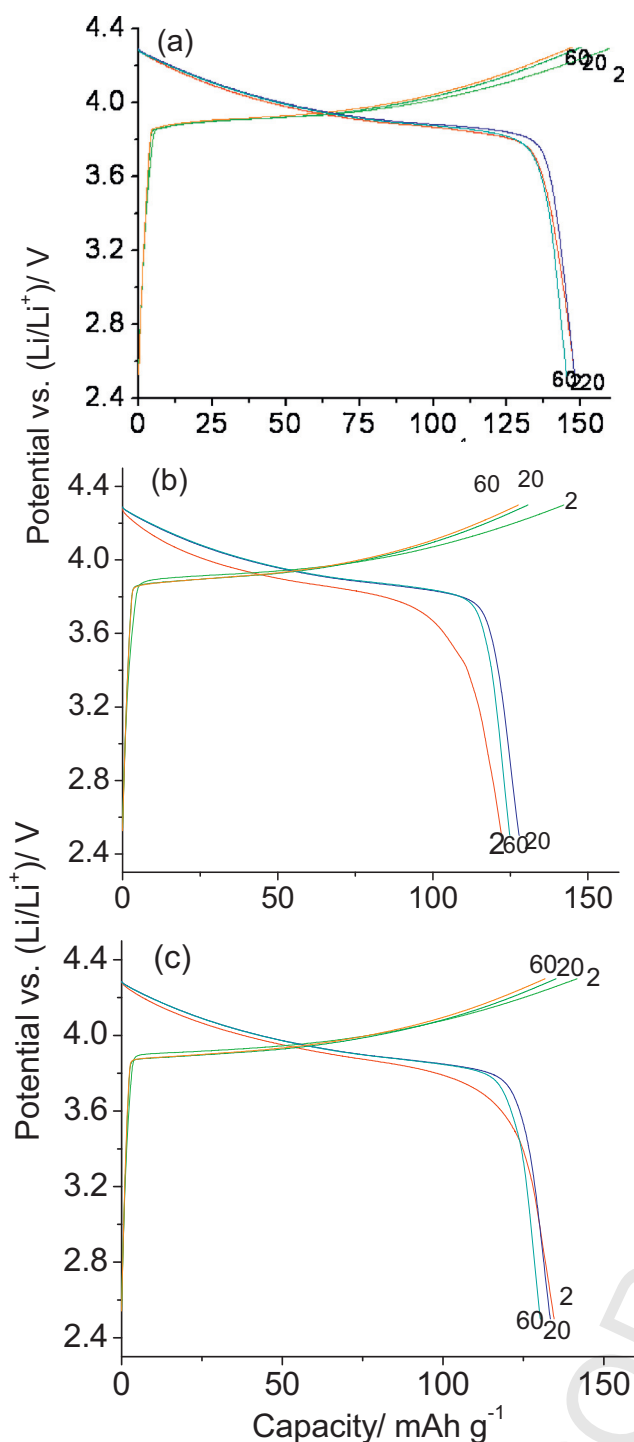
Cyclic voltammograms of the cells, in the range of 2.5–4.3 V at ambient temperature at a scan rate of  $0.058 \text{ mVs}^{-1}$  are shown in Figure 3 Figure 3. For clarity cyclic voltammograms of the second cycles of  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x=0, 0.03, 0.05$ ) are also shown in Figure 3. All compounds showed a main anodic peak at  $\sim 4.0 \text{ V}$  and the cathodic peak at  $\sim 3.8 \text{ V}$  correspond to  $\text{Co}^{3+/4+}$  redox couple [1,31]. The origin of a minor peak (anodic peak) at  $3.5 \text{ V}$  is not clear at present.

Galvanostatic cycling (charge and discharge) curves of bare and Mg-doped  $\text{LiCoO}_2$  are shown in Figure 4 Figure 4. During charging, Li-ions are removed from  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x=0, 0.03, 0.05$ ), hence Co undergoes oxidation from  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ . During discharging process, the reverse reaction occurs. We note Mg-ions are electrochemically inactive, are difficult to oxidize from  $\text{Mg}^{2+}$  to  $\text{Mg}^{3+}$  or  $\text{Mg}^{4+}$  and it act as conducting matrix. All compounds showed a plateau at  $3.9 \text{ V}$  vs. Li, which is similar to the observed curves in the CV. We note that the hexagonal structural transformations (Monoclinic  $\text{M} \rightarrow$  (Hexagonal)  $\text{H}_2$ , and  $\text{H}_2 \rightarrow \text{H}_3$ ) [1,33,34] are completely suppressed in both bare and doped  $\text{LiCoO}_2$ , this may lead to improved capacity retention during. The capacity vs. cycle number plots are shown in Figure 5 Figure 5. Irreversible capacity loss during 1<sup>st</sup> cycle was observed in all cases and ICL values are in the range, 25–30  $\text{mAh g}^{-1}$ . The cycling results clearly show that the  $\text{LiCoO}_2$  ( $x=0$ ) compound delivers a higher capacity compared to the other samples  $x=0.03$  and  $x=0.05$ , which is expected due to the Mg that is electrochemically inactive. The reversible capacity at the end of 20<sup>th</sup> are 150 ( $x=0$ ), 132 ( $x=0.03$ ) and 135 ( $x=0.05$ )  $\text{mAh g}^{-1}$  and corresponding capacity fading between 5 to 60 cycles are 3–6% (Table 1). The good cycling stability is due to a pure and well-ordered layered structure, with no cation mixing and uniform morphology as exemplified by the XRD analyses and SEM images and other reasons like improved conductivity. Maldinov et al. [18] reported sol-gel derived Mg-doped  $\text{LiCoO}_2$  showed a reversible capacity of 115 and 121  $\text{mAhg}^{-1}$  for bare and Mg-doped  $\text{LiCoO}_2$ , respectively and they showed 28 and 10% capacity loss up to 40 cycles, cycled in the voltage range, 2.9–4.3 V, at current rate of  $30 \text{ mA g}^{-1}$ . Levasseur et al. [19] reported a reversible capacities at 1<sup>st</sup> and 10<sup>th</sup> cycle, at current



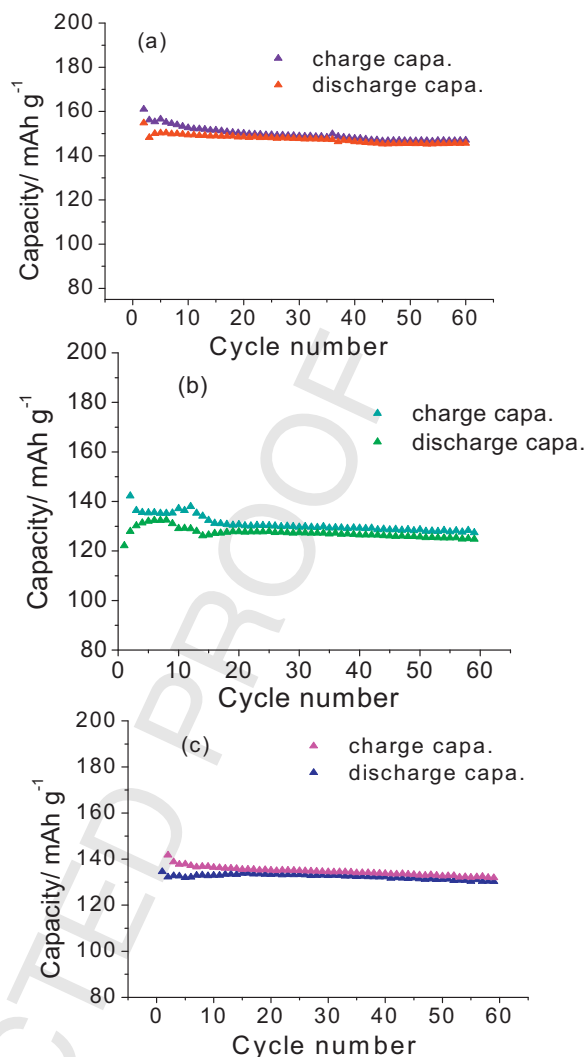
**Figure 3.** Cyclic voltammograms of  $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$  ( $x=0, 0.03, 0.05$ ): (a)  $\text{LiCoO}_2$ , (b)  $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$  and (c)  $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$ . Scan rate:  $0.058 \text{ mVs}^{-1}$ . Voltage range: 2.5–4.3 V vs. (Li/Li<sup>+</sup>). Only the 2<sup>nd</sup> cycle is shown for clarity.

rate of C/20, the voltage range, 2.7–4.15 V vs. Li are: 132 and 123  $\text{mAhg}^{-1}$  for  $x=0$ , 134 and 122  $\text{mAhg}^{-1}$  for  $x=0.03$  and 132 and 122 for  $x=0.05 \text{ mAhg}^{-1}$ . Kim et al. [35] reported  $x=0.03$  sample deliver a reversible capacity of  $130 \text{ mAhg}^{-1}$  at the end of 50<sup>th</sup> cycle, where as  $x=0$  sample deliver a reversible capacity of  $80 \text{ mAhg}^{-1}$  at the end of 50<sup>th</sup> cycle, when cycled in the voltage range of 3.0–4.3 V vs. Li and they prepared above mentioned samples using ball-milling followed by solid state reaction method. Sathiyamoorthi et al. [36] prepared using urea combustion/solid state method, they reported a reversible capacity of 96 and  $86 \text{ mAhg}^{-1}$  for  $x=0$  and  $x=0.2$ , cycled in the voltage range, 3.0–4.5 V. Microwave assisted bare and  $x=0.1$  doped  $\text{LiCoO}_2$  by Zaheena et al. [37] showed a



**Figure 4.** Graph of Voltage (V vs. (Li/Li<sup>+</sup>)) against Capacity (mAh/g): (a) LiCoO<sub>2</sub>, (b) Li(Mg<sub>0.03</sub>Co<sub>0.97</sub>)O<sub>2</sub> and (c) Li(Mg<sub>0.05</sub>Co<sub>0.95</sub>)O<sub>2</sub>, Voltage range, 2.5–4.3 V vs. Li; current rate: 30 mA g<sup>-1</sup>. For clarity 2, 20 and 60 cycles are shown.

reversible capacity of 85 and 125 mAhg<sup>-1</sup> at the end of 20<sup>th</sup> cycle, cycle at C/10 rate and in the voltage range, 2.5–4.2 V. Yin et al. [38] reported improved capacity retention with 1% Mg-doped LiCoO<sub>2</sub>, they showed about 81 and 85% capacity retention for bare and 1% Mg-doped LiCoO<sub>2</sub> after 50 cycles at current rate of 1 C, in the voltage range, 3.0–4.5 V. Very recently Nithya et al. [39] showed improved capacity with Cu, Mg co-doped LiCoO<sub>2</sub> and still capacity fading was not completely suppressed.



**Figure 5.** Graph of Capacity in (mAhg<sup>-1</sup>) against cycle number, (a) LiCoO<sub>2</sub>, (b) Li(Mg<sub>0.03</sub>Co<sub>0.97</sub>)O<sub>2</sub>, and (c) Li(Mg<sub>0.05</sub>Co<sub>0.95</sub>)O<sub>2</sub>, Voltage range, 2.5–4.3 V (Li/Li<sup>+</sup>); current rate: 30 mA g<sup>-1</sup>.

#### 4. Conclusions

The compounds, LiCoO<sub>2</sub>, Li(Mg<sub>0.03</sub>Co<sub>0.97</sub>)O<sub>2</sub> and Li(Mg<sub>0.05</sub>Co<sub>0.95</sub>)O<sub>2</sub> were prepared at 800 °C using the molten salt method. These samples were characterized using X-ray diffraction, scanning electron microscope and other electro-analytical techniques such as cyclic voltammetry and galvanostatic cycling. Galvanostatic cycling studies show LiCoO<sub>2</sub> delivering high and stable capacity of 147 mAhg<sup>-1</sup> at the end of the 60<sup>th</sup> cycle. Not much improvement were seen in the electrochemical performance of Mg-doped LiCoO<sub>2</sub> in comparison with the bare LiCoO<sub>2</sub> sample and further studies on the effect of the electrochemical performance of other Co/Mg-salts are in progress.

#### Acknowledgements

MVR thank to Council for Scientific & Industrial Research (CSIR), Pretoria, South Africa for sponsoring travel and accommodation grant to attend 13<sup>th</sup> ISE conference.



## References

- [1] K.S. Tan, M.V. Reddy, G.V. Subba Rao, B.V.R. Chowdari, High-performance LiCoO<sub>2</sub> by molten salt (LiNO<sub>3</sub>: LiCl) synthesis for Li-ion batteries, *J. Power Sources* 147 (2005) 241–248.
- [2] A. Sakunthala, M.V. Reddy, S. Selvasekarapandian, B.V.R. Chowdari, P.C. Selvin, Synthesis of compounds, Li(MMn<sub>11/6</sub>)O-4 (M = Mn-1/6, Co-1/6, (Co<sub>1/12</sub>Cr<sub>1/12</sub>), (Co<sub>1/12</sub>Al<sub>1/12</sub>), (Cr<sub>1/12</sub>Al<sub>1/12</sub>)) by polymer precursor method and its electrochemical performance for lithium-ion batteries, *Electrochim. Acta* 55 (2010) 4441–4450.
- [3] M. Prabu, M.V. Reddy, S. Selvasekarapandian, S. Admas, K.P. Loh, G.V. Subba Rao, B.V.R. Chowdari, Effect of LLT Coating on elevated temperature Cycle Life Performance of LiMn<sub>2</sub>O<sub>4</sub> Cathode Material, *Journal of Electrochemical Society* 160 (2013) A3144–A3147.
- [4] M.V. Reddy, H.Y. Cheng, J.H. Tham, C.Y. Yuan, H.L. Goh, B.V.R. Chowdari, Preparation of Li(Ni<sub>0.5</sub>Mn<sub>1.5</sub>)O-4 by polymer precursor method and its electrochemical properties, *Electrochim. Acta* 62 (2012) 269–275.
- [5] C.J. Jafta, M.K. Mathe, N. Manyala, W.D. Roos, K.I. Ozoemena, Microwave-Assisted Synthesis of High-Voltage Nanostructured LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> Spinel: Tuning the Mn<sup>3+</sup> Content and Electrochemical Performance, *ACS Appl. Mater. Interfaces* 5 (2013) 7592–7598.
- [6] K. Saravanan, M.V. Reddy, P. Balaya, H. Gong, B.V.R. Chowdari, J.J. Vittal, Storage performance of LiFePO<sub>4</sub> nanoplates, *J. Mater. Chem.* 19 (2009) 605–610.
- [7] C. Masquelier, L. Croguennec, Polyanionic, (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries, *Chem. Rev.* 113 (2013) 6552–6591.
- [8] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novak, Insertion electrode materials for rechargeable lithium batteries, *Adv. Mater.* 10 (1998) 725–763.
- [9] M.V. Reddy, G.V. Subba Rao, B.V.R. Chowdari, Metal Oxides, Oxyals as Anode Materials for Li Ion Batteries, *Chem. Rev.* 113 (2013) 5364–5457.
- [10] P. Verma, P. Maire, P. Novak, A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries, *Electrochim. Acta* 55 (2010) 6332–6341.
- [11] J.W. Fergus, Recent developments in cathode materials for lithium ion batteries, *J. Power Sources* 195 (2010) 939–954.
- [12] G. Ceder, Y.M. Chiang, D.R. Sadoway, M.K. Aydinol, Y.I. Jang, B. Huang, Identification of cathode materials for lithium batteries guided by first-principles calculations, *Nature* 392 (1998) 694–696.
- [13] P. Elumalai, H.N. Vasan, N. Munichandraiah, Microwave synthesis and electrochemical properties of LiCo<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> (M = Al and Mg) cathodes for Li-ion rechargeable batteries, *J. Power Sources* 125 (2004) 77–84.
- [14] H. Tukamoto, A.R. West, Electronic conductivity of LiCoO<sub>2</sub> and its enhancement by magnesium doping, *J. Electrochem. Soc.* 144 (1997) 3164–3168.
- [15] M.J. Zou, M. Yoshio, S. Gopukumar, J. Yamaki, Synthesis of high-voltage (4.5 V) cycling doped LiCoO<sub>2</sub> for use in lithium rechargeable cells, *Chem. Mater.* 15 (2003) 4699–4702.
- [16] M. Carewska, S. Scaccia, F. Croce, S. Arumugam, Y. Wang, S. Greenbaum, Electrical conductivity and Li-6, Li-7 NMR studies of Li<sub>1+y</sub>CoO<sub>2</sub>, *Solid State Ionics* 93 (1997) 227–237.
- [17] C.C. Chang, J.Y. Kim, P.N. Kumta, Divalent cation incorporated Li(1+x)MMg<sub>x</sub>O<sub>2</sub>(1+x) (M = Ni<sub>0.75</sub>Co<sub>0.25</sub>): viable cathode materials for rechargeable lithium-ion batteries, *J. Power Sources* 89 (2000) 56–63.
- [18] M. Mladenov, R. Stoyanova, E. Zhecheva, S. Vassilev, Effect of Mg doping and MgO-surface modification on the cycling stability of LiCoO<sub>2</sub> electrodes, *Electrochem. Commun.* 3 (2001) 410–416.
- [19] S. Levasseur, M. Menetrier, C. Delmas, On the Li<sub>x</sub>Co<sub>1-y</sub>Mg<sub>y</sub>O<sub>2</sub> system upon deintercalation: electrochemical, electronic properties and Li-7 MAS NMR studies, *J. Power Sources* 112 (2002) 419–427.
- [20] S. Levasseur, M. Menetrier, C. Delmas, On the dual effect of Mg doping in LiCoO<sub>2</sub> and Li<sub>1+δ</sub>CoO<sub>2</sub>: Structural, electronic properties, and Li-7 MAS NMR studies, *Chem. Mater.* 14 (2002) 3584–3590.
- [21] R. Thirunakaran, N. Kalaiselvi, P. Periasamy, N.G. Renganathan, Mg substituted LiCoO<sub>2</sub> for reversible lithium intercalation, *Ionics* 9 (2003) 388–394.
- [22] F. Nobili, S. Dsoke, F. Croce, R. Marassi, An ac impedance spectroscopic study of Mg-doped LiCoO<sub>2</sub> at different temperatures: electronic and ionic transport properties, *Electrochim. Acta* 50 (2005) 2307–2313.
- [23] M.V. Reddy, Z. Beichen, L.J. Nicholette, Z. Kaimeng, B.V.R. Chowdari, Molten Salt Synthesis and Its Electrochemical Characterization of Co<sub>3</sub>O<sub>4</sub> for Lithium Batteries, *Electrochem. Solid-State Lett.* 14 (2011) A79–A82.
- [24] M.V. Reddy, K.Y.H. Kenrick, T.Y. Wei, G.Y. Chong, G.H. Leong, B.V.R. Chowdari, Nano-ZnCo<sub>2</sub>O<sub>4</sub>(O<sub>4</sub>) Material Preparation by Molten Salt Method and Its Electrochemical Properties for Lithium Batteries, *J. Electrochem. Soc.* 158 (2011) A1423–A1430.
- [25] M.V. Reddy, X.W.V. Teoh, T.B. Nguyen, Y.Y.M. Lim, B.V.R. Chowdari, Effect of 0.5 M NaNO<sub>3</sub>: 0.5 M KNO<sub>3</sub> and 0.88 M LiNO<sub>3</sub>:0.12 M LiCl Molten Salts, and Heat Treatment on Electrochemical Properties of TiO<sub>2</sub>, *J. Electrochem. Soc.* 159 (2012) A762–A769.
- [26] X. Zhao, M.V. Reddy, H. Liu, S. Ramakrishna, G.V. Subba Rao, B.V.R. Chowdari, Nano LiMn<sub>2</sub>O<sub>4</sub> with spherical morphology synthesized by a molten salt method as cathodes for lithium ion batteries, *RSC Advances* 2 (2012) 7462–7469.
- [27] M.V. Reddy, C. Yu, F. Jiahuan, K.P. Loh, B.V.R. Chowdari, Molten salt synthesis and energy storage studies on CuCo<sub>2</sub>O<sub>4</sub> and CuO.Co<sub>3</sub>O<sub>4</sub>, *RSC Advances* 2 (2012) 9619–9625.
- [28] M. Prabu, M.V. Reddy, S. Selvasekarapandian, G.V. Subba Rao, B.V.R. Chowdari, Synthesis, impedance and electrochemical studies of lithium iron fluorophosphate, LiFePO<sub>4</sub>F cathode, *Electrochim. Acta* 85 (2012) 572–578.
- [29] M.V. Reddy, B.D. Tung, L. Yang, N.D. Quang Minh, K.P. Loh, B.V.R. Chowdari, Molten salt method of preparation and cathodic studies on layered-cathode materials Li(Co<sub>0.7</sub>Ni<sub>0.3</sub>)O<sub>2</sub> and Li(Ni<sub>0.7</sub>Co<sub>0.3</sub>)O<sub>2</sub> for Li-ion batteries, *J. Power Sources* 225 (2013) 374–381.
- [30] M. Nagarathinam, K. Saravanan, E.J.H. Phua, M.V. Reddy, B.V.R. Chowdari, J.J. Vittal, Redox-Active Metal-Centered Oxalato Phosphate Open Framework Cathode Materials for Lithium Ion Batteries, *Angewandte Chemie-International Edition* 51 (2012) 5866–5870.
- [31] S.L. Tey, M.V. Reddy, G.V. Subba Rao, B.V.R. Chowdari, J.B. Yi, J. Ding, J.J. Vittal, Synthesis structure, and magnetic properties of [Li(H<sub>2</sub>O)<sub>2</sub>M(N<sub>2</sub>H<sub>3</sub>CO<sub>2</sub>)(3)]center dot 0.5H<sub>2</sub>O (M = Co, Ni) as single precursors to LiMO<sub>2</sub> battery materials, *Chem. Mater.* 18 (2006) 1587–1594.
- [32] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. Sect. A: Found. Crystallogr.* A32 (1976) 751–767.
- [33] J.N. Reimers, J.R. Dahn, ELECTROCHEMICAL AND INSITU X-RAY-DIFFRACTION STUDIES OF LITHIUM INTERCALATION IN Li<sub>x</sub>COO<sub>2</sub>, *J. Electrochem. Soc.* 139 (1992) 2091–2097.
- [34] Z.H. Chen, J.R. Dahn, Methods to obtain excellent capacity retention in LiCoO<sub>2</sub> cycled to 4.5 V, *Electrochim. Acta* 49 (2004) 1079–1090.
- [35] H.J. Kim, Y.U. Jeong, J.H. Lee, J.J. Kim, Crystal structures, electrical conductivities and electrochemical properties of LiCo<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> (0 < x <= 0.11), *J. Power Sources* 159 (2006) 233–236.
- [36] R. Sathiyamoorthi, R. Chandrasekaran, P. Santhosh, K. Saminathan, R. Gangadharan, T. Vasudevan, Electrochemical characterization of nanocrystalline LiM<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> (M = Mg, Ca) prepared by a solid-state thermal method, *Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry* 36 (2006) 71–81.
- [37] C.N. Zaheena, C. Nithya, R. Thirunakaran, A. Sivashanmugam, S. Gopukumar, Microwave assisted synthesis and electrochemical behaviour of LiMg<sub>0.1</sub>Co<sub>0.9</sub>O<sub>2</sub> for lithium rechargeable batteries, *Electrochim. Acta* 54 (2009) 2877–2882.
- [38] R.Z. Yin, Y.S. Kim, S.J. Shin, I. Jung, J.S. Kim, S.K. Jeong, In Situ XRD Investigation and Thermal Properties of Mg Doped LiCoO<sub>2</sub> for Lithium Ion Batteries, *J. Electrochem. Soc.* 159 (2012) A253–A258.
- [39] C. Nithya, R. Thirunakaran, A. Sivashanmugam, S. Gopukumar, High-Performing LiMg<sub>x</sub>Cu<sub>y</sub>Co<sub>1-x-y</sub>O<sub>2</sub> Cathode Material for Lithium Rechargeable Batteries, *ACS Appl. Mater. Interfaces* 4 (2012) 4040–4046.