

Studies on Bare and Mg-doped LiCoO₂ as a cathode material for Lithium ion Batteries

M. V. Reddy^{1,2*}, Thor Wei Jie^{1,3}, Charl J. Jafta⁴, Kenneth I. Ozoemena^{4,5}, Mkhulu K. Mathe⁴,
A. Sree Kumaran Nair⁶, Soo Soon Peng⁷, M. Sobri Idris⁷, Geetha Balakrishna⁸, Fabian I.
Ezema⁹, B. V. R. Chowdari^{1*}

¹Department of Physics, Solid State Ionics & Advanced batteries lab, National University of Singapore,
Singapore 117542

²Department of Materials Science and Engineering, National University of Singapore, Singapore-117576

³Nanyang Junior College, 128 Serangoon Avenue 3, Singapore 556111

⁴Energy Materials, Materials Science & Manufacturing, Council for Scientific & Industrial Research, Pretoria
0001, South Africa

⁵Department of Chemistry, University of Pretoria, Pretoria, South Africa

⁶Amrita Centre for Nanosciences & Molecular Medicine, Amrita Institute of Medical Sciences, Amrita Vishwa
Vidyapeetham, Kochi-682041, Kerala, India

⁷School of Materials Engineering, Universiti Malaysia Perlis, Malaysia.

⁸Centre for Nano and Material Sciences, Jain University, Jakkasandra, Kanakapura, Bangalore rural-562112,
India

⁹Department of Physics and Astronomy, University of Nigeria, Nsukka

Corresponding authors: phymvvr@nus.edu.sg; phychowd@nus.edu.sg

Phone: 65162607; Fax: (65) 6777-6126

Abstract

In this paper, we report on the preparation of bare and Mg-doped Li(Mg_xCo_{1-x})O₂ (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 gcm⁻³, 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 LiCoO₂ show main cathodic and anodic redox peaks at ~ 3.9 V and ~ 4.0 V, respectively. Galvanostatic cycling of Li(Mg_xCo_{1-x})O₂ (x = 0, 0.03, 0.05) showed reversible charge capacity values at the 60th cycle to be: 147 (±3) mAh g⁻¹ (x = 0), 127 (±3) mAh g⁻¹ (x = 0.03), and 131 (±3) mAh g⁻¹ (x=0.05) cycled at a current density of 30 mA g⁻¹. Capacity retention is also favourable at 98.5 %.

Keywords: Molten salt method ; Mg-doped LiCoO₂ ; Cathode ; Electrochemical properties

1. Introduction

Commercial Lithium ion batteries (LIBs) consist of a LiCoO₂[1] or LiMn₂O₄[2, 3] LiNi_{0.5}Mn_{1.5}O₄[4, 5] or LiFePO₄[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 (LiCoO₂) due to its nice 4V 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 LiCoO₂ can deliver a reversible capacity of 120-140 mAhg⁻¹. 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 LiCoO₂ 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 LiCoO₂ can be improved by Mg-doping[14, 16-22]. In this project, Li(Mg_xCo_{1-x})O₂ (x = 0, x = 0.03, x = 0.05) compounds were prepared by the molten salt method (LiNO₃:LiCl eutectic as the molten salt) at 800 °C, and their cathodic performance was studied in a voltage range of 2.5-4.3V at current rate of 30 mA g⁻¹ for up to 60 charge-discharge cycles.

2. Experimental

Li(Mg_xCo_{1-x})O₂ (x = 0, 0.03, 0.05) samples were prepared at 800 °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 LiNO₃, 0.12 moles of LiCl, 1-x moles of (CH₃COO)₂Co and x moles of Mg(NO₃)₂ · 4H₂O were weighed and heated in an alumina crucible at 800 °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 °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 Li(Mg_xCo_{1-x})O₂ (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 °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 1M $\text{LiPF}_6(\text{EC};\text{DEC})$ (Merck) as a 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 °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 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 given in Table 1. The XRD patterns of $\text{Li}(\text{Co}_{1-x}\text{Mg}_x)\text{O}_2$ ($x = 0, 0.03, 0.05$) samples are similar to NaFeO_2 and no impurity lines of Co_3O_4 or MgO lines were observed. The obtained lattice parameter values are similar to reported literature on bare and doped LiCoO_2 by solid state method and other methods [14, 18]. In brief LiCoO_2 showed a lattice parameter values $a = 2.819$ (5) Å, $c = 14.052$ (8) Å [1, 31], Levasseur et al. reported a lattice parameter values of $a = 2.8212$ (1) Å, $c = 14.082$ (1) Å for $\text{LiCo}_{0.94}\text{Mg}_{0.06}\text{O}_2$ [20]. When doping with Mg^{2+} the Co^{3+} ions are substituted and therefore there will be a charge compensation mechanism (Co^{3+} to Co^{4+}) taking place or oxygen vacancies will be created which leads to structural defect stabilizing $\text{Co}^{3+(\text{IS})}$ ions. With the increase in Co^{4+} ions and intermediated spin $\text{Co}^{3+(\text{IS})}$ ions, there will be an enhancement in the conductivity compared to the un-doped LiCoO_2 [20]. Taking into account the ionic radii [32] of the Mg^{2+} (0.72 Å), Co^{3+} (0.545 Å) and 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 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), 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

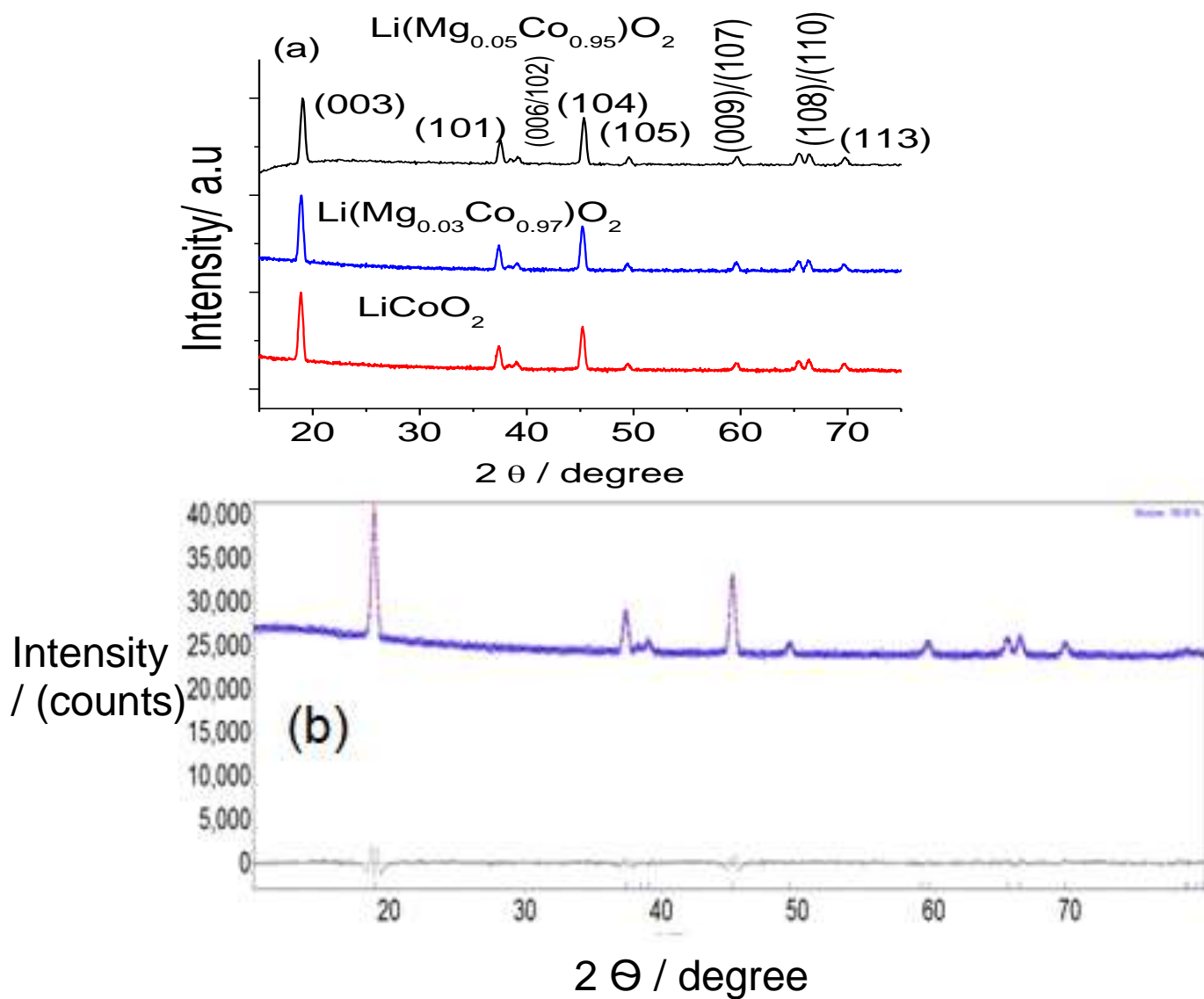


Figure 1: (a) XRD patterns of $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$ ($x = 0, 0.03, 0.05$) of all samples, (b) Rietveld refined X-ray diffraction pattern of LiCoO_2 synthesized using the molten salt method at 800°C . Vertical bars are Miller indices ($h k l$) as shown and indexed.

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

Compound	Lattice Parameter (\AA) and cell volume (V)= (\AA^3)	Theoretical Density (g/cm^3)	Experiment al Density (gcm^{-3})	BET Surface Area (m^2g^{-1})	Reversible capacity at 5 th and 60 th cycle (mAhg^{-1}), Capacity fading (5-60cyc.) %
$\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$					
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)

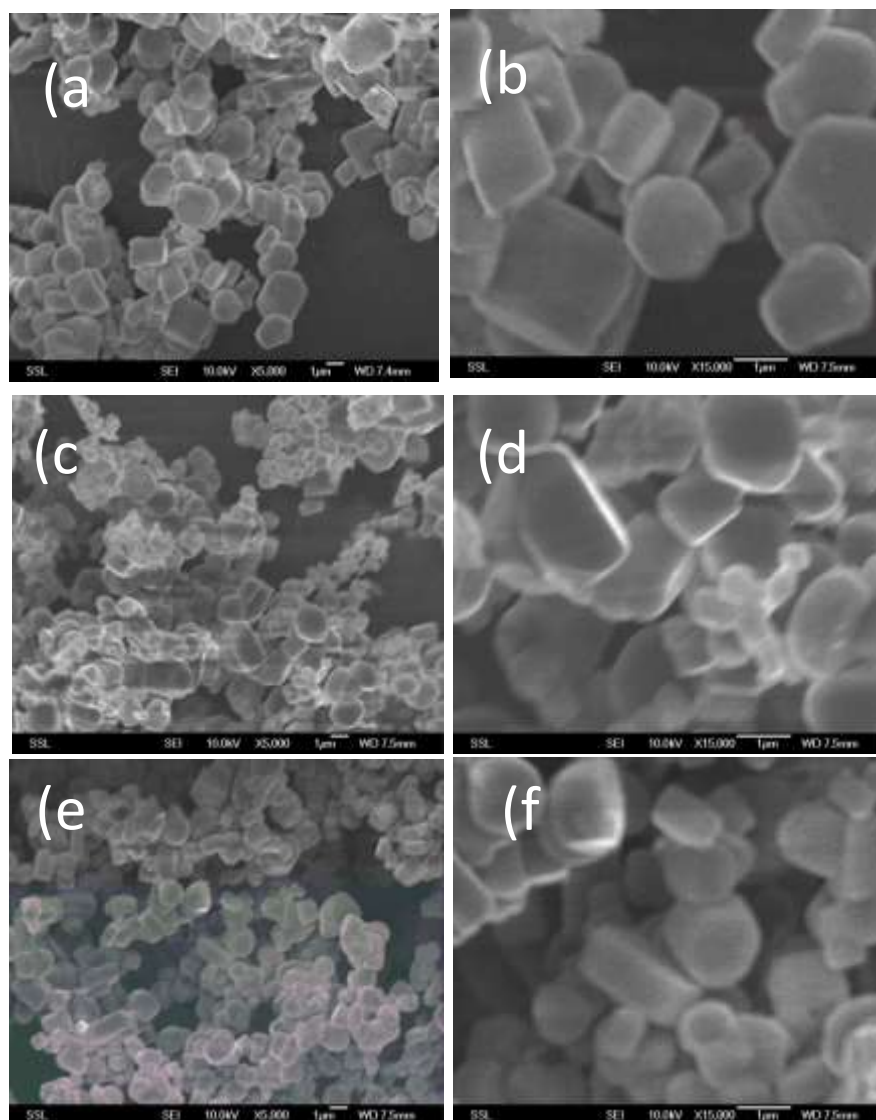


Figure 2: Scanning Electron micrographs of (a,b) LiCoO_2 , (c,d) $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$, (e,f) $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$ with two different magnifications bar scale, $1\ \mu\text{m}$.

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, $2\text{-}4\ \text{m}^2\text{g}^{-1}$ (Table1). The experimental density values are similar to the theoretical density values calculated from the XRD data.

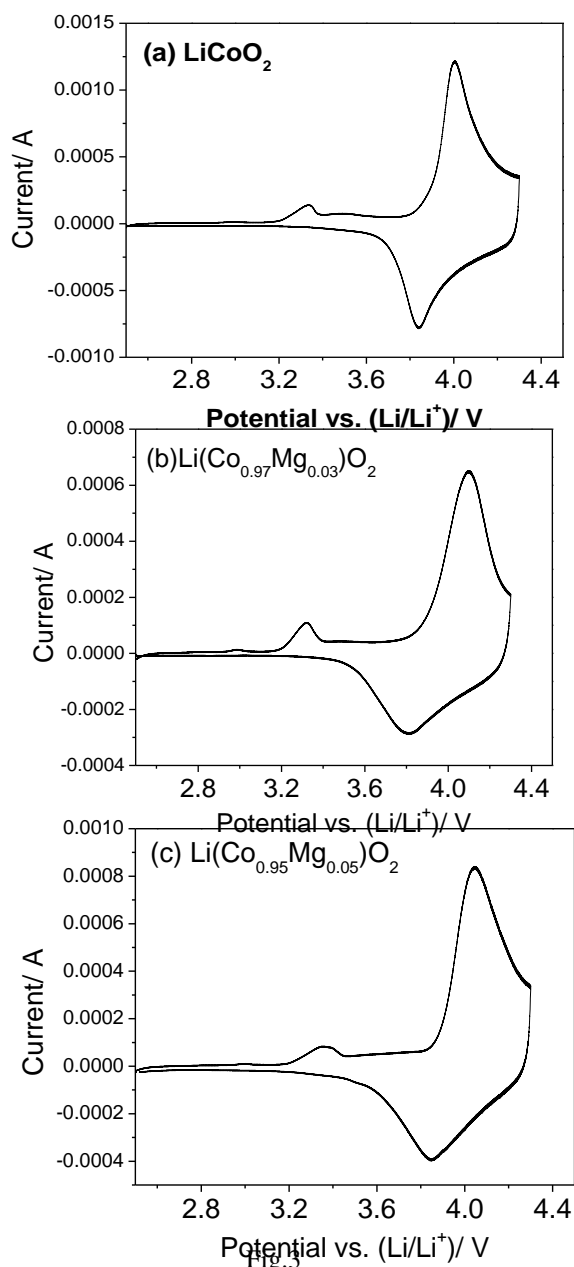


Figure 3: Cyclic voltammograms of $\text{Li}(\text{Mg}_x\text{Co}_{1-x})\text{O}_2$ ($x = 0, 0.03, 0.05$): (a) LiCoO_2 , (b) $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$ and (c) $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$. Scan rate: 0.058 mVs^{-1} . Voltage range: 2.5-4.3 V vs. (Li/Li^+) . Only the 2nd cycle is shown for clarity.

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 mVs^{-1} are shown in 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

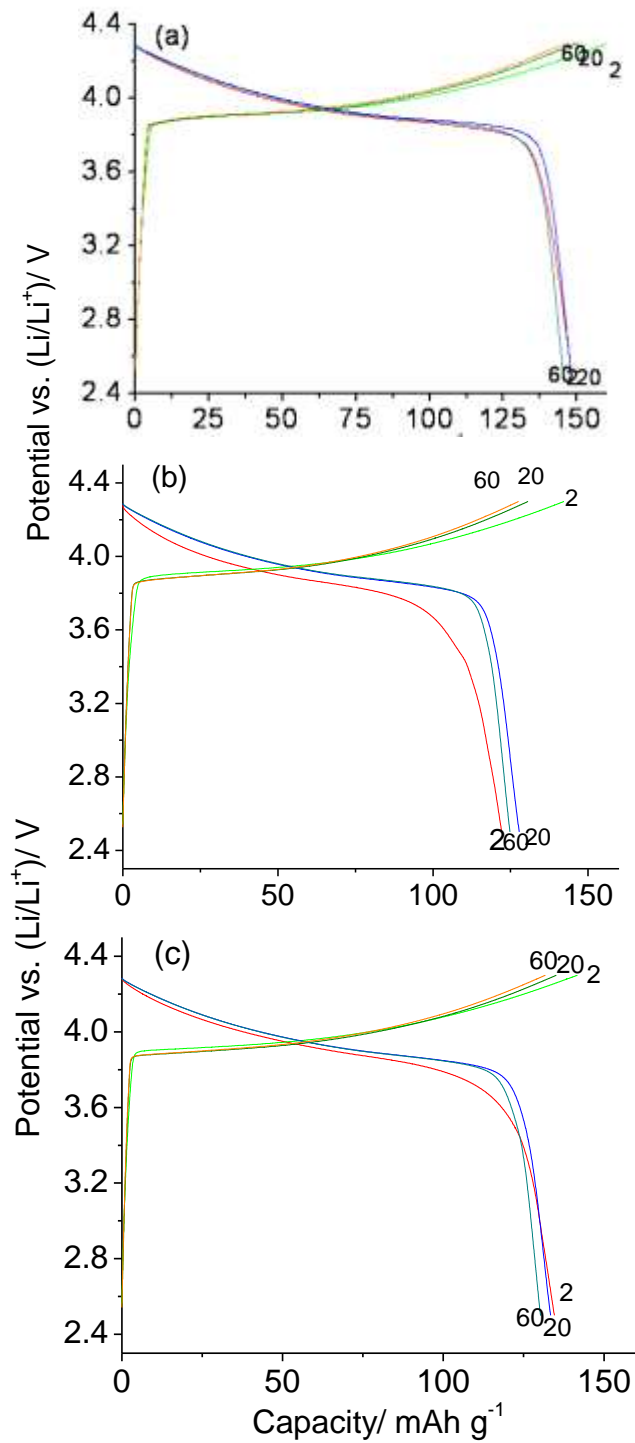


Figure 4: Graph of Voltage (V vs. (Li/Li⁺)) against Capacity (mAh/g): (a) LiCoO₂, (b) Li(Mg_{0.03}Co_{0.97})O₂ and (c) Li(Mg_{0.03}Co_{0.97})O₂, Voltage range, 2.5-4.3 V vs. Li ; current rate: 30 mA g⁻¹. For clarity 2, 20 and 60 cycles are shown.

compounds showed a main anodic peak at ~4.0 V and the cathodic peak at ~3.8 V correspond to $\text{Co}^{3+/4+}$ redox couple [1, 31]. The origin of a minor peak (anodic peak) at 3.5 V is not clear at present.

Galvanostatic cycling (charge and discharge) curves of bare and Mg-doped LiCoO_2 are shown in 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 Co^{3+} to Co^{4+} . During discharging process, the reverse reaction occurs. We note Mg- ions are electrochemically inactive, are difficult to oxidize from Mg^{2+} to Mg^{3+} or Mg^{4+} and it act as conducting matrix. All compounds showed a plateau at 3.9 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) H_2 , and $\text{H}_2 \rightarrow \text{H}_3$) [1, 33, 34] are completely suppressed in both bare and doped LiCoO_2 , this may leads to improved capacity retention during. The capacity vs. cycle number plots are shown in Figure 5. Irreversible capacity loss during 1st cycle was observed in all cases and ICL values are in the range, 25-30 mAh g^{-1} . The cycling results clearly show that the 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 electrochemical inactive. The reversible capacity at the end of 20th are 150 ($x=0$), 132 ($x=0.03$) and 135 ($x=0.05$) mAh g^{-1} and corresponding capacity fading between 5 to 60 cycles are 3-6 % (Table1). 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 LiCoO_2 showed a reversible capacity of 115 and 121 mAh g^{-1} for bare and Mg-doped LiCoO_2 , respectively and they showed 28 and 10 % capacity loss up to 40 cycles, cycled in the voltage range, 2.9-4.3V, at current rate of 30 mA g^{-1} . Levasseur et al. [19] reported a reversible capacities at 1st and 10th cycle, at current rate of C/20, the voltage range, 2.7-4.15V vs. Li are: 132 and 123 mAh g^{-1} for

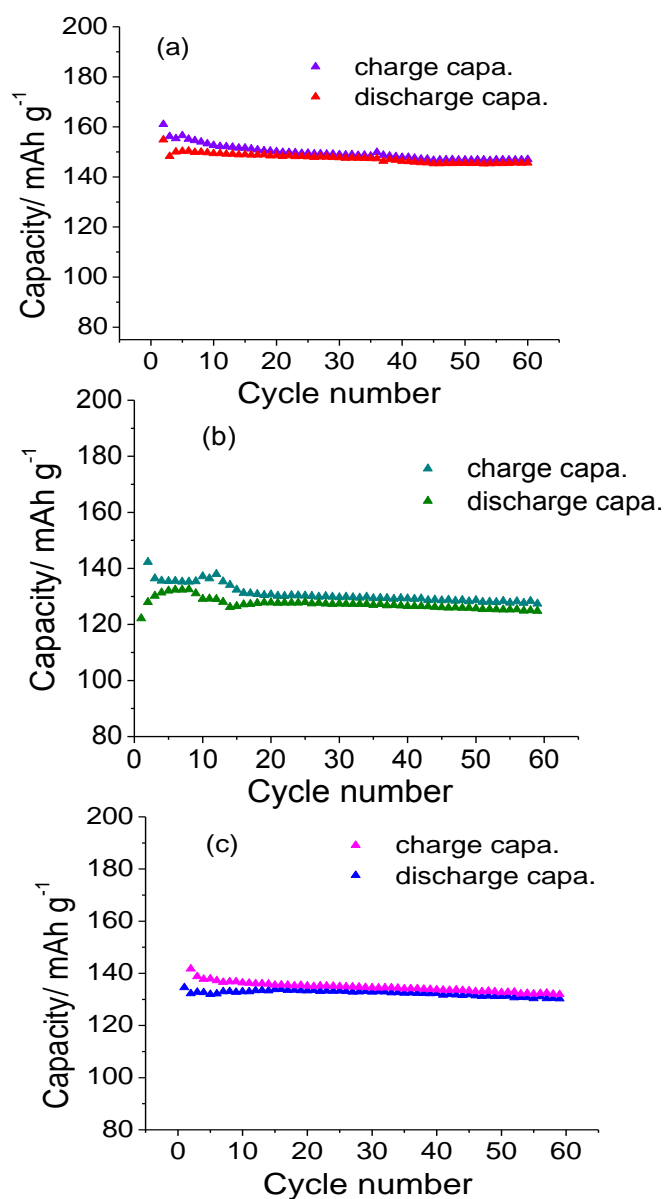


Figure 5: Graph of Capacity in (mAhg^{-1}) against cycle number, (a) LiCoO_2 , (b) $\text{Li}(\text{Mg}_{0.03}\text{Co}_{0.97})\text{O}_2$, and (c) $\text{Li}(\text{Mg}_{0.05}\text{Co}_{0.95})\text{O}_2$, Voltage range, 2.5-4.3 V (Li/Li^+); current rate: 30 mA g^{-1} .

$x=0$, 134 and 122 mAhg^{-1} for $x=0.03$ and 132 and 122 for $x=0.05$ mAhg^{-1} . Kim et al. [35] reported $x=0.03$ sample deliver a reversible capacity of 130 mAhg^{-1} at the end of 50th cycle, where as $x=0$ sample deliver a reversible capacity of 80 mAhg^{-1} at the end of 50th cycle,

when cycled in the voltage range of 3.0-4.3V 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 mAhg⁻¹ for x=0 and x=0.2, cycled in the voltage range, 3.0-4.5V. Microwave assisted bare and x=0.1 doped LiCoO₂ by Zaheena et al. [37] showed a reversible capacity of 85 and 125 mAhg⁻¹ at the end of 20th cycle, cycle at C/10 rate and in the voltage range, 2.5-4.2V. Yin et al. [38] reported improved capacity retention with 1% Mg -doped LiCoO₂, they showed about 81 and 85 % capacity retention for bare and 1% Mg-doped LiCoO₂ after 50 cycles at current rate of 1C, in the voltage range, 3.0-4.5V. Very recently Nithya et al.[39] showed improved capacity with Cu, Mg co-doped LiCoO₂ and still capacity fading was not completely suppressed.

4. Conclusions

The compounds, LiCoO₂, Li(Mg_{0.03}Co_{0.97})O₂ and Li(Mg_{0.05}Co_{0.95})O₂ 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 LiCoO₂ delivering high and stable capacity of 147 mAhg⁻¹ at the end of the 60th cycle. Not much improvement were seen in the electrochemical performance of Mg-doped LiCoO₂ in comparison with the bare LiCoO₂ 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 13th ISE conference.

REFERENCES

- [1] K.S. Tan, M.V. Reddy, G.V. Subba Rao, B.V.R. Chowdari, High-performance LiCoO₂ by molten salt (LiNO₃ : 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_{11/6})O₄ (M = Mn-1/6, Co-1/6, (Co_{1/12}Cr_{1/12}), (Co_{1/12}Al_{1/12}), (Cr_{1/12}Al_{1/12})) 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 LiMn₂O₄ 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_{0.5}Mn_{1.5})O₄ 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_{1.5}Ni_{0.5}O₄ Spinel: Tuning the Mn³⁺ 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 LiFePO₄ 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 and Oxysalts 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_{1-x}M_xO₂ (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 LiCoO₂ 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 LiCoO₂ 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_{1+y}CoO₂, *Solid State Ionics* 93 (1997) 227-237.
- [17] C.C. Chang, J.Y. Kim, P.N. Kumta, Divalent cation incorporated Li_(1+x)MMg_xO_{2(1+x)} (M = Ni_{0.75}Co_{0.25}): 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 LiCoO₂ electrodes, *Electrochem. Commun.* 3 (2001) 410-416.
- [19] S. Levasseur, M. Menetrier, C. Delmas, On the Li_xCO_{1-y}Mg_yO₂ 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 LiCoO₂ and Li_{1+delta}CoO₂: 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 LiCoO₂ 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 LiCoO₂ 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 Co₃O₄ 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-ZnCo₂O₄ 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 NaNO₃: 0.5 M KNO₃ and 0.88 M LiNO₃:0.12 M LiCl Molten Salts, and Heat Treatment on Electrochemical Properties of TiO₂, *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 LiMn₂O₄ 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 CuCo₂O₄ and CuO.Co₃O₄, *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, LiFePO₄F 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_{0.7}Ni_{0.3})O₂ and Li(Ni_{0.7}Co_{0.3})O₂ 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(H₂O)M(N₂H₃CO₂)(₃)]center dot

- 0.5H₂O (M = Co,Ni) as single precursors to LiMO₂ 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_xCOO₂, *J. Electrochem. Soc.* 139 (1992) 2091-2097.
- [34] Z.H. Chen, J.R. Dahn, Methods to obtain excellent capacity retention in LiCoO₂ 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_{1-x}Mg_xO₂ (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_xCo_{1-x}O₂ (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_{0.1}Co_{0.9}O₂ 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 LiCoO₂ for Lithium Ion Batteries, *J. Electrochem. Soc.* 159 (2012) A253-A258.
- [39] C. Nithya, R. Thirunakaran, A. Sivashanmugam, S. Gopukumar, High-Performing LiMg_xCu_yCo_{1-x-y}O₂ Cathode Material for Lithium Rechargeable Batteries, *ACS Appl. Mater. Interfaces* 4 (2012) 4040-4046.