

Cite this: *RSC Advances*, 2012, 2, 11574–11577

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PAPER

Solar powered lithium-ion battery incorporating high performing electrode materials†

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Received 20th April 2012, Accepted 27th September 2012

DOI: 10.1039/c2ra21999a

The development of portable electronic communities requires high performing and high power lithium rechargeable batteries. Herein, we explore a new lithium ion battery combined with a new carbon based anode and cobalt based cathode which delivers an energy output of 280 Wh kg^{−1} and cycling efficiency of 97% over the investigated 500 cycles (1 C rate) of the lithium ion cell.

Introduction

The commercialization of lithium ion cells was achieved in the early 1990's by the Sony Corporation. Almost 90% of commercial lithium ion batteries consist of a lithium cobalt oxide cathode¹ and a graphite anode, which is separated by a lithium ion conducting electrolyte, for example 1 M LiPF₆ in 1 : 1 (ethylene carbonate : diethylene carbonate). Only 5–10% of the lithium ion cells are made by using LiFePO₄ or LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ based cathodes and carbon based anodes. The commercial success of lithium ion batteries is still limited at high voltages and high rates because of the lack of suitable electrode materials for this application. Tin based amorphous oxide anode materials exhibit a high capacity for storing Li⁺ ions as reported by Y. Yu *et al.*² Recently TiO₂³ and carbon nanotube⁴ based anode materials exhibiting high capacities have been reported by various research groups. However, a large volume change during cycling can destroy the anode structure, resulting in poor retention capacity for prolonged cycling. With this in mind, researchers still focus on graphite based anode materials like graphene,^{5,6} which exhibits excellent capacity and cyclability.

Besides this, the cathode material also limits the storage capacity of rechargeable lithium batteries. K. Kang *et al.*⁷ reported that the safe, inexpensive LiNi_{0.5}Mn_{0.5}O₂ cathode material delivers a discharge capacity of 125 mAhg^{−1} at 1 C rate. Recently Recham *et al.*⁸ reported LiFeSO₄F cathode materials exhibiting good capacity retention, however, the voltage (3.6 vs. Li) is lower than for LiCoO₂. Iron and manganese based phosphate materials such as LiFePO₄^{9–12} and LiCo_xMn_{1–x}PO₄¹³ have drawn attention for use in lithium ion batteries; however, these materials have problems like conduc-

tivity and lower voltage, which is overcome by carbon coating and nano-sized particles. LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ surrounded by a concentration gradient outer layer exhibits high capacity, but after 50 cycles the capacity fades very rapidly as reported by Y. K. Sun *et al.*¹⁴ Due to the above shortcomings, researchers still focus on LiCoO₂ cathode materials because it has a high theoretical capacity and high voltages compared to the above mentioned materials; however, it delivers half of the theoretical capacity, and is also expensive. Various methods to overcome these shortcomings, such as coating with inactive metal oxides¹⁵ and doping with metal cations,^{16,17} improve the capacity in the limited voltage regions (~4.3 V), but this strategy fails at the deep discharge states as reported by many researchers. Deepa *et al.*¹⁸ and M. Zou *et al.*¹⁹ reported that the conductivity of LiCoO₂ was enhanced by Cu and operates well at 4.5 V delivering high capacity retention. Increasing the potential to >4.5 V requires a suitable dopant to increase the structural stability as well as cycling stability at high voltages. Mg is the most promising dopant to stabilize the layered structure of LiCoO₂ as reported by many authors.^{20–23} The presently used lithium ion cells deliver an energy output of 100–250 Wh kg^{−1} and a cycling efficiency only 80–90%.²⁴ To overcome the above problems in electrode materials and lithium ion cells, we have developed a new lithium ion cell comprising of a graphite paper anode and Cu, Mg doped LiCoO₂ cathode.

Results and discussion

Fig. 1 shows the XRD patterns of the carbon paper and LiMg_{0.025}Cu_{0.175}Co_{0.8}O₂ materials. XRD patterns of the carbon paper indicate that the presence of a graphitic structure, and the cathode material clearly shows a layered structure in the R3m space group. The clear splitting of the (006) (102) (Fig. 1c) and (108) (110) (Fig. 1d) peak doublets indicates that an ordered distribution of lithium and transition metal ions exist in the structure.²⁵ Unit cell parameters of the synthesized materials are calculated by using X'Pert high score plus software. Lattice parameters 'a' (2.816), 'c' (14.057) and unit cell volume (96.087)

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c2ra21999a

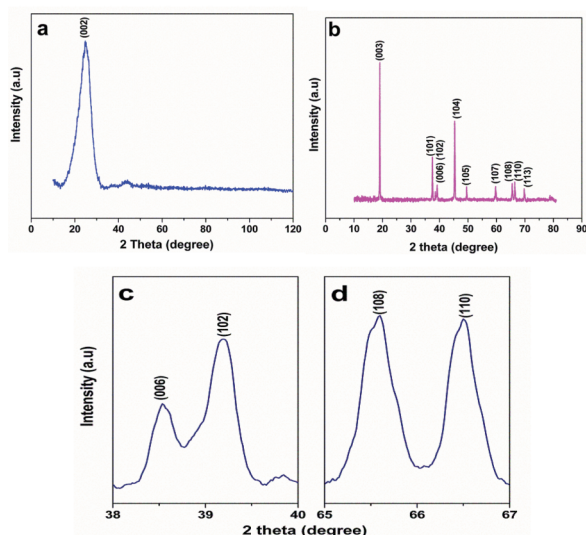


Fig. 1 a) XRD patterns of carbon paper and b) $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ materials. Magnified patterns of c) (006) (102) and d) (108) (110) peak doublets.

increase after doping with Cu and Mg in LiCoO_2 . The c/a (4.991) ratio > 4.9 , $I_{003}/I_{104} > 1$ and 'R' value (0.34) suggest the formation of a well developed layered structure. Fig. 2 depicts the SEM images of carbon paper and $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ materials. The anode material exhibits a microfibre type morphology and the cathode material appears like a bunch of flakes. This kind of anode and cathode morphology could easily extract and insert the lithium ions during charge and discharge. The size of the flakes is around $0.5\ \mu\text{m}$.

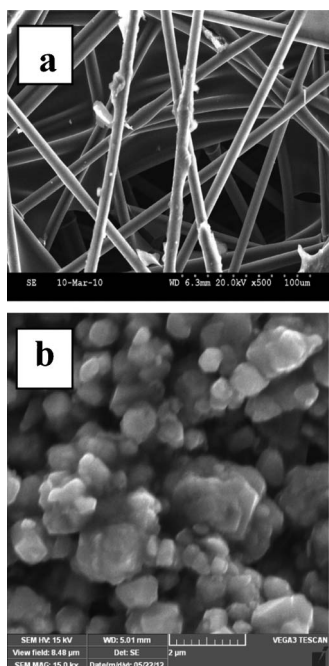


Fig. 2 SEM images of a) carbon paper and b) $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ materials.

Fig. 3a shows the first charge/discharge curves and cycling performance of carbon paper (vs. Li/Li^+) at 0.2 and 1 C rates cycled between 0.01–1.5 V. The carbon paper delivers a discharge capacity of 225 and 100 mAh g^{-1} at a rate of 0.2 and 1 C respectively. A very low irreversible capacity ($< 5\ \text{mAh g}^{-1}$) is obtained in both cases, which is due to the formation of a very thin SEI layer, which consumes a small amount of Li^+ ions. This charge/discharge process is coupled with intercalation and deintercalation of lithium into the layers of carbon. Fig. 3b presents the cycling performance of carbon paper; at the end of the 100th cycle it retains 95 and 96% of the initial capacity at a rate of 0.2 and 1 C respectively. This excellent cycling stability is due to the formation of a thin SEI layer on the initial cycle, which assists the movement of Li^+ ions in the subsequent cycles.

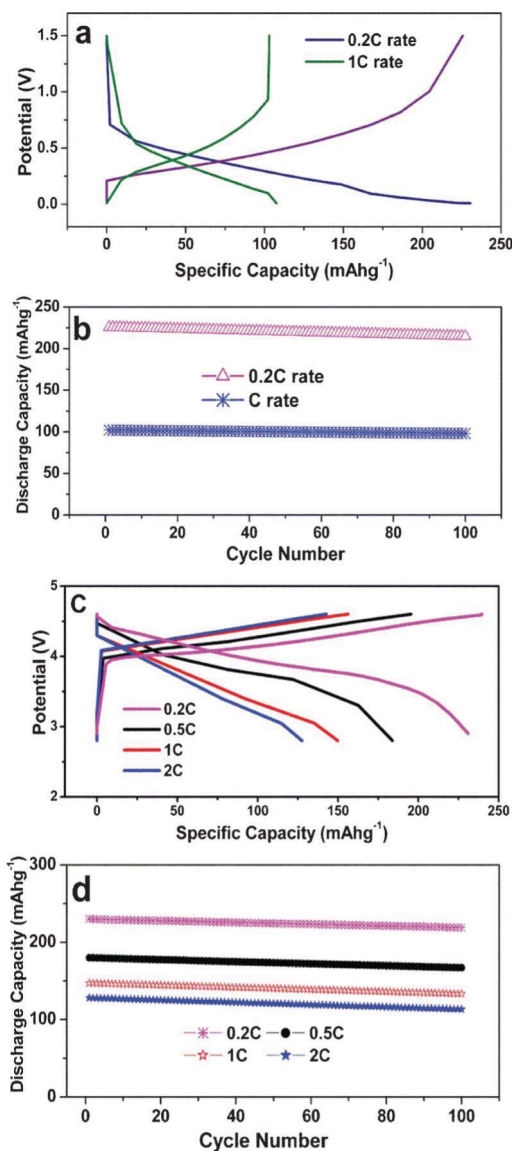


Fig. 3 a) Initial charge/discharge curves of carbon paper at a rate of 1 C and 0.2 C cycled between 0.01–1.5 V b) Cycling performance of carbon paper c) Initial charge/discharge curves of $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ at different rates cycled between 2.9–4.6 V d) Cycling performances of $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ materials at different C rates.

This shows excellent cycling stability at high rates in comparison to previous works.^{3–6}

The charge/discharge curves and cycling performance of the $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ material (vs. Li/Li^+) at different C rates cycled between the potential limits 2.9–4.6 V are shown in Fig. 3c. This material delivers the initial discharge capacities of 230, 180, 147 and 128 mAhg^{-1} at 0.2 C, 0.5 C, 1 C and 2 C rates respectively. In this material, 0.826 Li^+ and 0.798 Li^+ ions are extracted and re-inserted in the first cycle, after prolonged cycling the extraction and insertion amount of Li^+ ions decreases very slightly. The highest capacity of this material is ascribed to the increase of structural stability and conductivity of Mg^{2+} ions (Fig. 5). Furthermore, the dopant Cu^{2+} ions also completely participate in the redox reactions (Fig. 6). The larger ionic radii of Cu^{2+} and Mg^{2+} ions compared to Co^{3+} increases the lattice volume, which is favorable for intercalation and de-intercalation of Li^+ ions. In general, when the cell was cycled at high voltages,

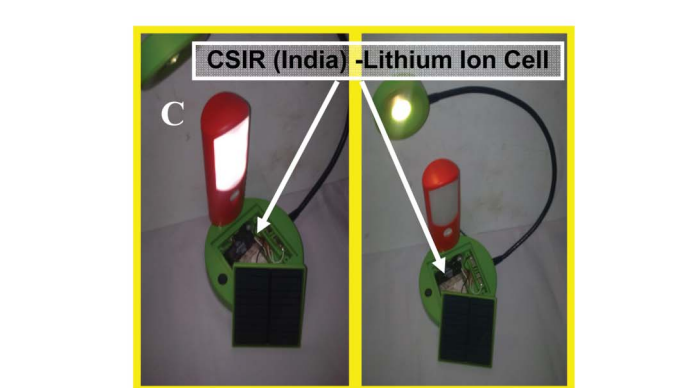
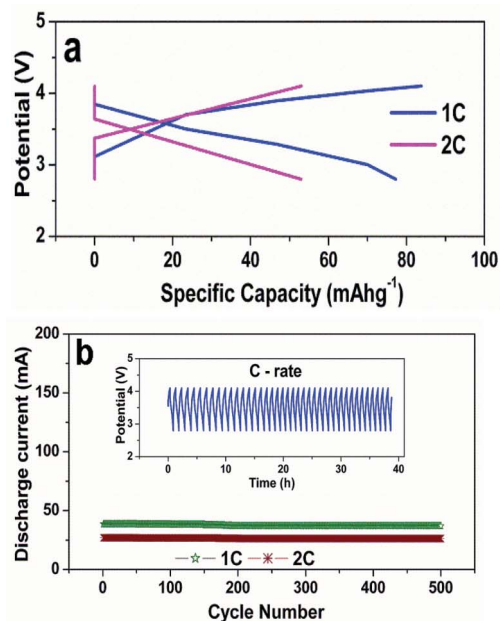


Fig. 4 a) Charge/discharge curves of the lithium ion cell at 1 C and 2 C rates. b) Cycling performance of the lithium ion cell at 1 C and 2 C rates over 500 cycles. Inset shows the cycling behaviour of the lithium ion cell at 1 C rate. c) Assembled lithium ion pouch cell charged by solar power used to activate LED lights.

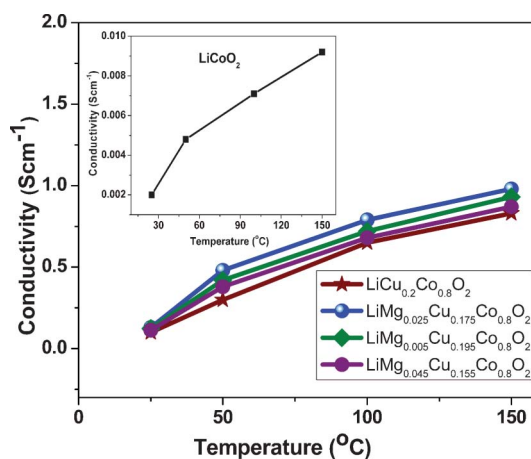


Fig. 5 Conductivity measurements of $\text{LiMg}_x\text{Cu}_y\text{Co}_{1-x-y}\text{O}_2$ materials.

it could extract and insert a large amount of Li^+ ions and also the redox event takes place completely. Fig. 3d depicts the cycling performance of this material at different C rates; the capacity retention obtained at 0.2, 0.5 C, 1 C and 2 C rates are 95.2, 92.3, 90.1, and 89.32 respectively over the investigated 100 cycles. It is interesting to note that the discharge capacities are higher and the capacity fade is very minimal at high voltage and high discharge rates as compared to the previous reports.^{8,9,12–14,18–23,26–31} This excellent retention capacity of Cu and Mg doped materials is due to the structural stability of the layered $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ materials enhanced by Mg^{2+} addition. The Mg^{2+} ions are electrochemically inactive, however, Mg^{2+} ions act as pillars to prevent the collapse of the CoO_2 interlayer and also do not hinder the lithium ion diffusion because it has a similar ionic radii to Li^+ ions. Furthermore, Mg^{2+} suppresses Co^{4+} ion dissolution in the electrolyte due to the stronger Mg–O bond than Co–O bond. This kind of pillar effect affords more space for Li^+ ions during cycling and offers excellent cycling stability.

To investigate the performance of the above-mentioned two electrode materials in a lithium ion cell we assembled the coin cell using carbon paper as the anode, $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ as the cathode and 1 M LiPF_6 in 1 : 1 EC/DEC as the electrolyte. Fig. 4a presents the charge/discharge behaviour of the lithium ion cell at 1 C and 2 C rates. The discharge capacities are 38 (specific discharge capacity 77 mAhg^{-1}) and 27 mAh (specific discharge capacity 55 mAhg^{-1}) at 1 C and 2 C rates when cycled

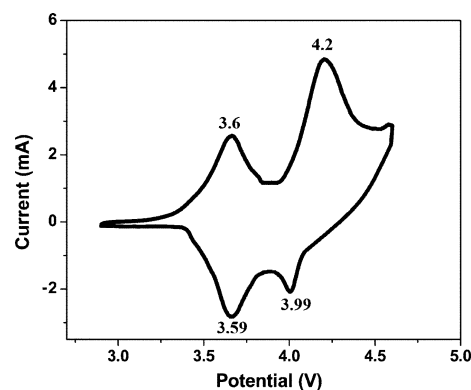


Fig. 6 Cyclic voltammogram of $\text{LiMg}_{0.025}\text{Cu}_{0.175}\text{Co}_{0.8}\text{O}_2$ material.

between 2.9–4.2 V. Fig. 4b shows the cycling performance of the lithium ion cell over the 500 cycles and the inset presents the cycling behaviour at 1 C rate. The capacity retention over the investigated 500 cycles is 96 and 97.5% at 1 C and 2 C rates respectively. The highest capacity retention is due to the pillaring effect of dopant ions in the cathode materials and the structure of the carbon paper also supports repeated lithium insertion and de-insertion. It delivers an energy output of 280 Wh kg⁻¹ (average specific capacity per kilogram $\times$ average cell voltage = 75.5 Ah kg⁻¹ $\times$ 3.7 V = 280 Wh kg⁻¹), the charge/discharge efficiency is 97% at both C rates. Fig. 4c shows glowing LED lights (16 LEDs) using this assembled lithium ion cell powered by solar power. The assembled lithium ion cell can be charged either by means of solar or normal charging. This excellent performance is superior to the presently used lithium ion cells,²⁴ which have an energy output of 100–250 Wh kg⁻¹ and the charge/discharge efficiency is 80–90%. The fade in capacity of this lithium ion cell after 500 cycles is only 4% at 1 C rate, which is superior compared to previously reported work incorporating Sn–C anode and Li[Ni_{0.45}Co_{0.1}Mn_{1.45}]O₄ as cathode, which exhibits a capacity fade of 14%.³¹

To further confirm the highest discharge capacity of the LiMg_{0.025}Cu_{0.175}Co_{0.8}O₂ cathode materials in the lithium ion battery we carried out conductivity measurements and cyclic voltammetry studies. The electronic conductivity of the cathode material is very important for a better charge transfer process during lithium intercalation/de-intercalation processes in the lithium ion cell. The electrical conductivity of the synthesized materials was determined by using a four-probe DC method from a set of voltage–current values using a power source controlled by a PC. The values were obtained by taking $\sigma = 1/\rho$, $\rho = RA/L$ where L is the distance between voltage contacts and A is the sample cross section. Fig. 5 shows the electronic conductivities of the LiCoO₂, LiCu_{0.2}Co_{0.8}O₂ and LiMg_{0.025}Cu_{0.175}O₂ materials at different temperatures. While the temperature increases from 25 to 150 °C, the conductivity of material increases and hence the conductivity of both Cu and Mg doped materials is two orders of magnitude higher than the pristine LiCoO₂ material. Fig. 6 shows the cyclic voltammogram of LiMg_{0.025}Cu_{0.175}O₂ material carried out between the potential limits 2.9 and 4.6 V. Two pairs of redox peaks observed for LiMg_{0.025}Cu_{0.175}O₂ material which is the characteristic behaviour of Li⁺ ion intercalation and de-intercalation. Redox peaks are observed for Cu²⁺/Cu⁺ ions at 3.6 and 3.59 V, which is in agreement with previous works.³² The above obtained results confirm that the highest capacity of LiMg_{0.025}Cu_{0.175}O₂ material is due to the highest conductivity of Mg²⁺ ions (which also enhance the structural stability by the pillaring effect) and Cu²⁺ ions which completely participate in the redox reactions.

Conclusions

In conclusion, we have developed a new high performing lithium ion battery combined with new anode and cathode materials which can be charged by solar power. These materials are very suitable for making solar powered lithium ion batteries. Anode and cathode materials (vs. Li) deliver a capacity retention of 96% (100 cycles) and 90.1% (100 cycles) at 1 C rate respectively. The lithium ion cell exhibits an energy output of 270 Wh kg⁻¹, where

the charge/discharge efficiency is 97%, and 97.5% capacity retention could be obtained even at high rates (2 C) over the investigated 500 cycles. Suitable anode and cathode materials enhance power and cycling life of the rechargeable lithium batteries.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research (CSIR), India for support of this work under the TAPSUN project of CSIR.

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