

Surface modification of nanocrystalline LiCoO₂ particles with rare earth oxides using polymeric resin process

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ABSTRACT

Nanocrystalline LiCoO₂ particles were prepared using ethylene glycol assisted Pechini process and rare earth oxides (Sm₂O₃ and La₂O₃) coated nanocrystalline LiCoO₂ particles were prepared using newly developed polymeric resin process. The prepared particles were characterized using TG/DSC, FTIR, XRD, SEM and XRF. The electrical conductivities were evaluated through impedance measurements for the pure, Sm₂O₃ and La₂O₃ coated nanocrystalline LiCoO₂ particles.

Keywords: Nanocrystalline LiCoO₂ particles, Surface modification, XRD, FTIR, SEM, XRF, Impedance spectroscopy, Electrical Conductivity.

1. INTRODUCTION

There is a great demand for energy storage devices, such as rechargeable batteries. Among the family of rechargeable batteries, Li-ion batteries have been an increasing potential applications in portable electronic devices due to their high energy density and high specific capacity [1]. Among the available positive electrode materials, layer structured LiCoO₂ is the most preferred electrode used in commercial Li-ion batteries because of its high theoretical capacity (274 mAhg⁻¹) [2-5]. However, LiCoO₂ exhibits a capacity fading at high rates due to its structural instability and reactivity with electrolyte. During charge and discharge process, Li_{1-x}CoO₂ undergoes a phase transition from hexagonal to monoclinic, if x value exceeds 0.5 and hence, leads to capacity fade [6]. In order to mitigate this problem, attempts have made through coating of metal oxides over LiCoO₂ particles [7-10]. The coating reduces the direct contact with electrolyte and protects the original structure during charging/discharging process. In the present work, newly developed polymeric resin process was used for coating of rare earth oxides (Sm₂O₃, La₂O₃) over LiCoO₂ nanoparticles. The prepared rare earth oxides (Sm₂O₃, La₂O₃) coated LiCoO₂ powders were characterized using TG/DSC, FTIR, XRD, SEM and XRF techniques. The electrical conductivities were evaluated through impedance measurements for

pure, Sm₂O₃ and La₂O₃ coated nanocrystalline LiCoO₂ particles.

2. EXPERIMENTAL

LiNO₃(s.d fine), Co(NO₃)₂.6H₂O (Qualigens), citric acid anhydrous (Qualigens) and ethylene glycol (merck chemicals) were used for the synthesis of nanocrystalline LiCoO₂ particles by Pechini process. Required quantities of metal nitrate, citric acid and ethylene glycol solutions were prepared separately and mixed by keeping total metal ion to citric acid and ethylene glycol ratio as 1 : 1 : 1 under stirring condition. The mixed solution was evaporated at 80°C to remove excess water. After 6-8 hours, it has turned into viscous resin. Further, the resin was heated at 150°C for 12 hours to obtain the polymeric intermediate. The polymeric intermediate was grounded and calcined at 500°C for 12 hours to obtain LiCoO₂ nanoparticles.

For Sm₂O₃ and La₂O₃ coating over LiCoO₂ particles, polyacrylic acid (LR grade, National chemicals), ethylene glycol (merck), samarium nitrate (AR grade, CDH), lanthanum nitrate (SRL chemicals,) and nanocrystalline LiCoO₂ particles were used. The required quantity of LiCoO₂ particles were dispersed in acetone and sonicated for 30 minutes to remove the agglomerations and then acetone was removed by drying in hot air oven. The obtained dried LiCoO₂ particles were dispersed in ethanol through sonication (A). The 10 : 2 molar ratio of polyacrylic acid and ethylene glycol solutions were mixed under constant stirring. The obtained clear solution was evaporated at 80°C to remove excess water. Stoichiometric amounts of samarium nitrate / lanthanum nitrate solution was added to the PAA and EG solution under constant stirring to maintain the molar ratio of total metal ions to PAA and EG as 1 : 10 : 2. Further evaporation, leads to the formation of polymeric resin (B). A and B were mixed under vigorous stirring and the evaporation was continued for 6 hours. Finally, black coloured solid mass was obtained and was calcined at 500°C for 6 hours to obtain Sm₂O₃ / La₂O₃ coated LiCoO₂ nanoparticles.

TG/DSC curves of the polymeric resins of Sm₂O₃ and La₂O₃ coated nanocrystalline LiCoO₂ samples were recorded at the heating rate of

10⁰C for minute between 30⁰C and 600⁰C using TA instrument SDT Q600 V20.5. FTIR spectra were recorded using shimadzu FTIR-8000 spectrometer. Powder X-ray diffraction patterns were recorded using X'pert PRO MPD, PANalytical (Philips) X-ray powder diffractometer with Cu K α radiation of wavelength 1.54 Å at a scan rate of 2⁰ per minute. The microstructures of all the prepared samples were imaged using scanning electron microscope (Hitachi, S-3400N model). The percentage of elements present in the samples were examined using X-ray fluorescence spectrometry (Bruker S4 Pioneer model). The impedance data of all the prepared samples were recorded using Novacontrol Alpha A high performance frequency analyzer.

3. RESULTS AND DISCUSSION

3.1. TG / DSC

TG/DSC curves of Sm₂O₃ and La₂O₃ polymeric resins coated LiCoO₂ nanoparticles are shown in fig.1 a, b. From fig.1a, the observed weight loss about 1.3% in TG curve between 30⁰C and 130⁰C is due to the removal of adsorbed moisture and the weight loss about 2 % between 170⁰C and 435⁰C is due to the decomposition of organic derivatives as well as removal of nitrates. The respective exothermic peaks were observed in DSC curve. TG curve does not show any more weight loss above 500⁰C, which indicates the complete removal of volatiles, nitrates and organic derivatives from the polymeric resin.

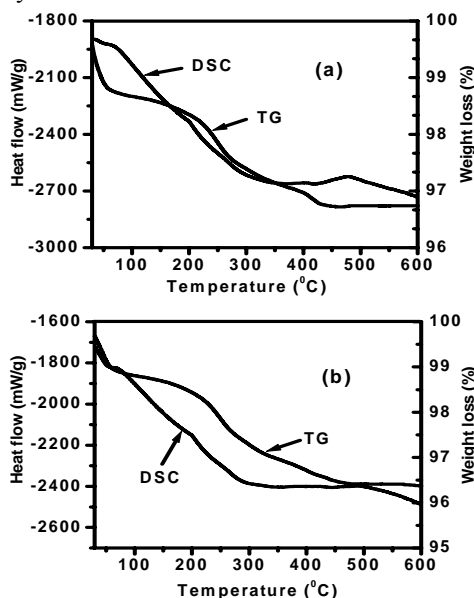


Fig.1 TG/DSC curves of a) Sm₂O₃ and b) La₂O₃ coated LiCoO₂ polymeric resins.

From fig.1 b, the weight loss about 1.2 % between 30⁰C and 130⁰C is due to the removal of

adsorbed moisture and the respective endothermic peak was observed in DSC curve. The weight loss about 2.3 % between 150⁰C and 465⁰C with two exothermic peaks in DSC curve indicates the decomposition of organic derivatives as well as removal of nitrates.

3.2 FTIR

FTIR spectra of bare, resin, Sm₂O₃ and La₂O₃ coated LiCoO₂ nanoparticles are shown in fig.2 a, b. From fig.2 a, b, bare LiCoO₂ exhibited three peaks at 510 cm⁻¹, 550-560 cm⁻¹ and 580-610 cm⁻¹ and correspond to the asymmetric stretching modes of [CoO₆] octahedra in LiCoO₂ [11]. For resin coated LiCoO₂, the observed IR peaks at 1577 cm⁻¹ and 1475 cm⁻¹ correspond to the asymmetric stretching modes of COO⁻ groups. The sharp IR peak at 1384 cm⁻¹ corresponds to NO₃⁻ ions [12-13]. The band between 1020-1220 cm⁻¹ is due to the stretching vibration of C-O-C groups [14].

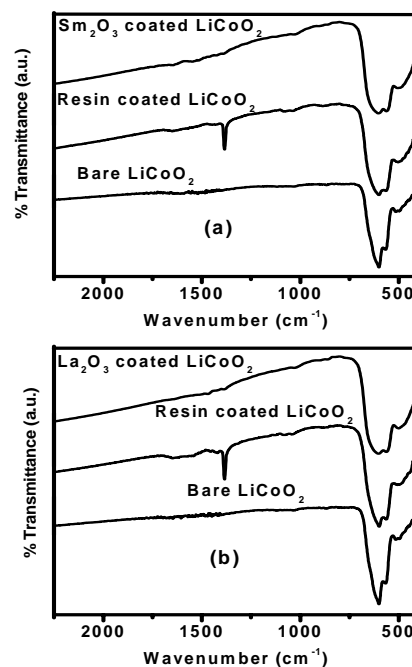


Fig.2 FTIR spectra of a) bare and resin, Sm₂O₃ coated LiCoO₂ and b) bare and resin, La₂O₃ coated LiCoO₂ particles.

For Sm₂O₃ coated LiCoO₂, the observed IR peaks at 530 cm⁻¹ and 610 cm⁻¹ attributed to the stretching modes of Sm₂O₃ structure and the shifting and broadening of the peaks at 550-560 cm⁻¹ and 580-610 cm⁻¹ are due to the formation of Sm₂O₃ coated LiCoO₂ structure. For La₂O₃ coated LiCoO₂, the observed peaks at 450 cm⁻¹ and 640 cm⁻¹ assigned to the stretching mode of La-O from La₂O₃ structure [15]. The shifting and broadening of the band at 580-610 cm⁻¹ may be due to the formation of La₂O₃ coated LiCoO₂ structure.

3.3 XRD

The XRD patterns of bare, resin, Sm_2O_3 and La_2O_3 coated LiCoO_2 nanoparticles are shown in fig.4a,b. From fig.3 a,b, the XRD patterns of the polymeric resin, Sm_2O_3 and La_2O_3 coated LiCoO_2 particles did not exhibit any extra new peaks corresponding to Sm_2O_3 and La_2O_3 phases, which indicates that the coating may be in an amorphous phase. Also, XRD patterns of bare, Sm_2O_3 and La_2O_3 coated LiCoO_2 nanoparticles indicate that coating of oxides did not effect the crystalline phase of the LiCoO_2 nanoparticles, which is confirmed by comparing the observed XRD peaks with standard JCPDS data.

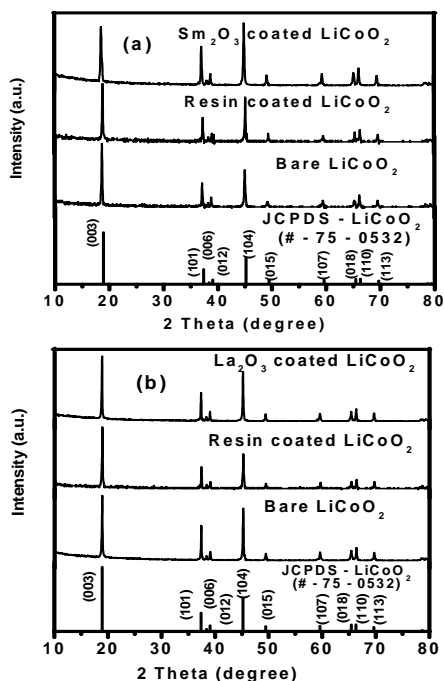


Fig.3 XRD patterns of a) bare, Sm_2O_3 polymeric resin and Sm_2O_3 coated LiCoO_2 and b) bare, La_2O_3 polymeric resin and La_2O_3 coated LiCoO_2 particles.

3.4 SEM

SEM micrographs of Sm_2O_3 and La_2O_3 coated

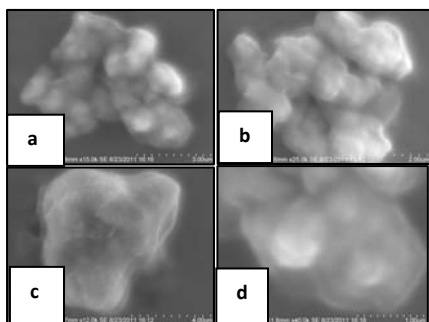


Fig.4 SEM micrographs of Sm_2O_3 coated LiCoO_2 (a,b) and La_2O_3 coated LiCoO_2 particles (c,d).

LiCoO_2 nanoparticles at different magnifications are shown in fig.4a-d. Fig.4 a-b, show the SEM images of the Sm_2O_3 coated LiCoO_2 particles. Fig.4 c-d, show the SEM images of La_2O_3 coated LiCoO_2 particles. All images show a very thin nano size layer over the agglomerated LiCoO_2 nanoparticles, which may be due to Sm_2O_3 and La_2O_3 coating over the agglomerated LiCoO_2 nanoparticles.

Further, presence of Sm_2O_3 and La_2O_3 in Sm_2O_3 and La_2O_3 coated LiCoO_2 nanoparticles are confirmed from the elemental analysis of the measured XRF spectra.

3.5. XRF

XRF spectra of Sm_2O_3 and La_2O_3 coated LiCoO_2 nanoparticles are shown in fig. 5a,b. From fig.5a,b, the presence of Sm_2O_3 , La_2O_3 and CoO in Sm_2O_3 and La_2O_3 coated LiCoO_2 particles are confirmed from the observed characteristic peaks.

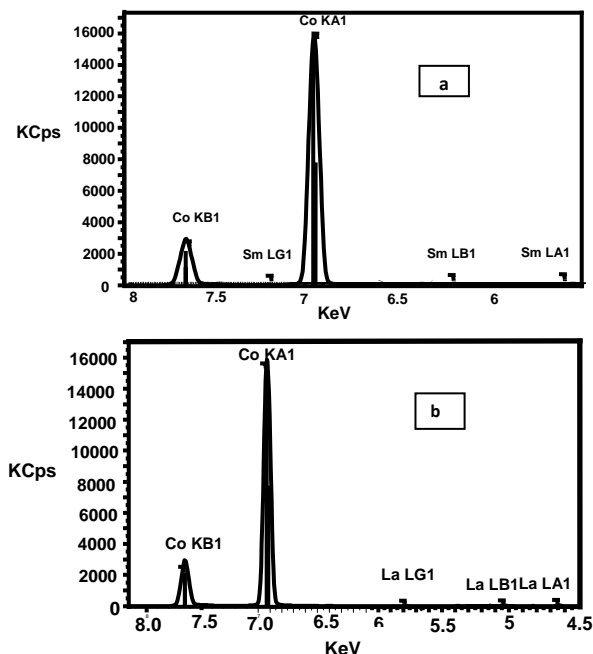


Fig.5 XRF spectra of a) Sm_2O_3 coated LiCoO_2 and b) La_2O_3 coated LiCoO_2 particles.

Lithium is not detected, since it is a light element. So, excluding the percentages of Sm_2O_3 , La_2O_3 and CoO , the remaining percentage corresponds to the presence of Li_2O . The Sm_2O_3 , La_2O_3 and CoO percentages are given in the table 1. Hence, XRF results confirm the presence of Sm_2O_3 , La_2O_3 and CoO in Sm_2O_3 and La_2O_3 coated LiCoO_2 nanoparticles.

Material	CoO	Sm ₂ O ₃	La ₂ O ₃
Sm ₂ O ₃ coated LiCoO ₂	83.930	1.849	
La ₂ O ₃ coated LiCoO ₂	84.980		1.810

Table 2. Percentages of CoO, Sm₂O₃ and La₂O₃ exist in Sm₂O₃ and La₂O₃ coated LiCoO₂ nanoparticles.

3.6. Electrical Conductivity Studies

Fig.6 shows the impedance plots of bare, Sm₂O₃ and La₂O₃ coated LiCoO₂ nanoparticles. From fig.6, the observed two overlapped semicircles were analyzed using win fit software. The first and second semi circles indicate the grain interior and grain boundary effects respectively [16]. The grain interior (R_{gi}) and the grain boundary (R_{gb}) resistances of bare, Sm₂O₃ and La₂O₃ coated LiCoO₂ sample pellets sintered at 200⁰C for half an hour are obtained respectively from the intercepts of first and second semicircles with the real axis. The evaluated electrical conductivities of bare, Sm₂O₃ and La₂O₃

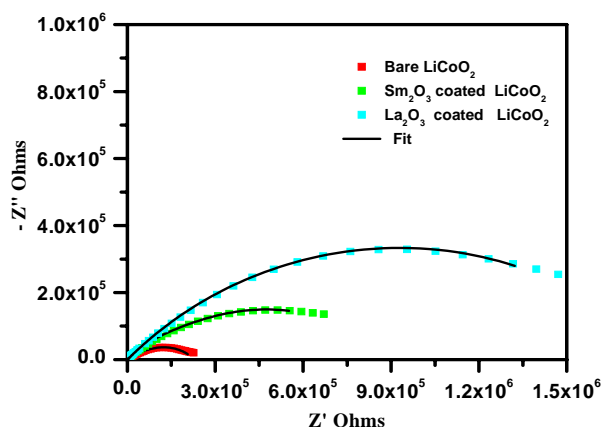


Fig.6 Impedance (Z' and $-Z''$) plots of bare, Sm₂O₃ and La₂O₃ coated nanocrystalline LiCoO₂ particles.

coated LiCoO₂ particles are found to be $6.597 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$, $4.766 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $4.336 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ respectively. It is observed that the conductivities of Sm₂O₃ and La₂O₃ coated LiCoO₂ particles are less compared to bare LiCoO₂, which may be due to the presence of nanosize Sm₂O₃ and La₂O₃ layers over the LiCoO₂ particles. The nano size Sm₂O₃ and La₂O₃ layers protect the LiCoO₂ structure during charge/discharge, which may enhance the capacity retention.

4. CONCLUSION

Nanocrystalline LiCoO₂ and Sm₂O₃, La₂O₃ coated LiCoO₂ particles were synthesized using Pechini and

novel polymeric resin processes respectively. Formation of [CoO₆], Sm₂O₃ and La-O of La₂O₃ structures are confirmed from FTIR spectral results. The amorphous nature of the Sm₂O₃ and La₂O₃ layers over LiCoO₂ particles are confirmed from the observed XRD results. The presence of Sm₂O₃, La₂O₃ and CoO are confirmed from XRF results. The Sm₂O₃ and La₂O₃ coated LiCoO₂ particles are found to have less conductivity, compared to bare LiCoO₂ particles.

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REFERENCES

- (1) Nazri, A.; Pistoia, G. Lithium batteries: Science and technology, Kluwer: Boston, 2004; p 1.
- [2] L.D. Dyer, B.S. Borie Jr., G.P. Smith, J. Am. Chem. Soc. 76 (1954)1499.
- [3] J.M. Tarascon, M. Armand, Nature (London) 414 (2001) 359.
- [4] C. Julien, S. Gastro-Garcia, J. Power Sources 97–98 (2001) 290.
- [5] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novák, Adv. Mater. 10 (1998)725.
- [6] J. Cho, Y.J. Kim, T.J. Kim, B. Park, Angew. Chem. Int. Ed. 40 (2001)3367.
- [7] Y. J. Kim, H. Kim, B. Kim, D. Ahn, J. G. Lee, T. J. Kim, D. Son, J. Cho, Y. W. Kim, and B. Park, Chem. Mater. 15 (2003) 1505.
- [8] S. Oh, J. K. Lee, D. Byuna, W. I. Cho, and B. W. Cho, J. Power sources, 132 (2004) 249.
- [9] B. Kim, J. G. Lee, M. Choi, J. Cho, and B. Park, J. Power sources, 126 (2004) 190.
- [10] J. Kim, M. Noh, J. Cho, H. Kim, and K. B. Kim, J. Electrochem. Soc. 152 (2005) A1142.
- [11] R. Ganesan, S. Vivekanandhan, T. Gnanasekaran, G. Periaswami, and R. S. Srinivasa, J. Nucl. mate. 325 (2004) 134.
- [12] G. Socrates, Infrared and Raman Characteristic Group Frequencies, John Wiley and Sons, New York (2001).
- [13] Y. M. Hon, K. Z. Fung, S. P. Lin, and M. H. Hon, J. Solid state Chem. 163 (2002) 231.
- [14] K. J. Rao, H. B. Moudden, B. Desbat, P. Vinatier, and A. Levasseur, J. Solid State Chem. 165 (2002) 42.
- [15] R. A. El-mallawany, Infrared phys. 29 (1989) 781.
- [16] C. Tian, Siu-Wai Chan, Solid State Ionics 134 (2000) 89.