

PEO/LaCoO₃ Composite Polymer Electrolyte and Its Electrochemical Properties

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Abstract. Composite polymer electrolyte film composed of polyethylene oxide (PEO) polymer matrix and LaCoO₃ as filler was prepared by solution casting method. LaCoO₃ perovskite was synthesized by sol-gel Schiff base method. The electrochemical properties of LaCoO₃ were studied by using cyclic voltammetry and the conductivity of the composite polymer was obtained from the electrochemical impedance spectroscopy (EIS). Cyclic voltammogram of LaCoO₃ film in 1 M KCl electrolyte showed the reduction peaks of Co³⁺ and Co²⁺ at 0.8 V and 0.5 V respectively. Electrochemical Impedance Spectra of PEO:LaCoO₃ composite polymer showed increase of charge transport which due to the mobility of the cobalt species. The conductivity of PEO/LaCoO₃ polymer electrolyte is enhanced compared to that of PEO. The prepared electrolyte is expected to be used for solid polymer electrolyte in metal air battery.

Keywords: PEO, LaCoO₃, polymer electrolyte, EIS, ionic conductivity

1. Introduction

Solid polymer electrolyte (SPE) has attracted very much attention for applications in energy storage devices for example, batteries of different types and laptop computers. Alkaline solid polymer electrolytes based on PEO have been used for battery systems [1,2]. The advantages of using SPE replacing liquid electrolytes is flexible, no leakage and low self discharge in batteries. The most frequent used polymer is polyethylene oxide (PEO) because it can dissolve many alkaline salts MX and benefit structure for supporting ion migration. However this polymer showed low ionic conductivity in the range of 10⁻⁷ S cm⁻¹ to 10⁻⁸ S cm⁻¹ which restricted the mobility of ions. Attempts have been made to increase ionic conductivity of PEO. Plasticizers such as PEG [3], dimethyl carbonate and diethyl carbonate [4] were added to polymer electrolytes to improve their conductivities. Attention has been paid to nanosize ceramic materials as filler to enhance the conductivity of polymer electrolytes. The addition of ceramic filler into polymer matrix results in reducing the glass transition temperature (T_g) and increase the amorphous phases of polymer matrix, therefore increase the ionic conductivity. Different inorganic fillers such as bentonite, TiO₂ and Al₂O₃ and mesoporous materials i.e. ZSM-5 molecular sieves were also used to disperse in polymer electrolytes. Xueli Li employed LiAl-SBA, a kind of mesoporous molecular sieve containing lithium as filler added into PEO electrolyte, the conductivity of PEO is enhanced greatly by adding LiAl-SBA compared with PEO/LiClO₄ and PEO/LiClO₄/nano-SiO₂ composite electrolytes [5]. ABO₃ perovskite-type of metal oxide also receives a lot of focus because of their properties i.e. superconductivity, piezoelectricity and catalytic activity [6]. Enhancing the ionic conductivity of PEO based plasticized composite polymer electrolyte by using LaMnO₃ nanofiller was studied by T. Kuila [7]. LaCoO₃ is an ABO₃ perovskite type which has been used as a catalyst in the cathode for fuel cell. In this work, we report the preparation of LaCoO₃ by Schiff base method and used as a filler for PEO polymer electrolyte. The electrochemical impedance spectroscopy was used to investigate the electrochemical properties of the polymer electrolyte prepared.

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2. Experimental

2.1 Preparation of LaCoO₃

LaCoO₃ was synthesized by Schiff base sol gel method as reported by Worayingyong [8]. Mixture of 25 ml 0.3M La(NO₃)₃(99% BDH), 25 ml 0.3M Co(NO₃)₃(99% Univar) and 4.71 ml salicyldehyde (98% Fluka) were refluxed until temperature increase to 55°C. Then 2.01 ml Etheylinediamine (99% Fluka) was added and refluxed for 3 hrs. The mixture of LaCoO₃ sol was then dried at 65 °C and calcined at 700 °C for 5 hrs.

The resulting LaCoO₃ powder was characterized by X-ray Diffraction (XRD, Philips: X'Pert) using Cu Kα (30.0 KV current 15 mA) scan rate of 0.5 deq / min. For LaCoO₃ film preparation, the LaCoO₃ sol (before drying) was coated on the FTO by dipping method.

2.2 Preparation of composite polymer electrolyte

A 0.5 grams of polyethylene oxide (PEO) was mixed with 10 ml of acetonitrile and 5 ml of ethanol, stirred for 30 mins until all PEO dissolved. For LaCoO₃-PEO composite electrolyte, 0.004 grams of LaCoO₃ was added to the PEO solution and kept stirring for another one hours. The polymer electrolyte was coated on the FTO substrate by casting method.

2.3 Electrochemical characterizations

Cyclic voltammetric measurement of LaCoO₃ film was performed in 1M KCl, Ag/AgCl and Pt rod were used as reference (REF) and counter (CE) electrodes respectively. For EIS measurements, two FTO blocking electrodes were used to sandwich the polymer film. A series of impedance measurements at different applied voltages from 0, 0.2, 0.5 and 0.8 V were obtained by using Potentiostat (PG 302N Auto lab) in the frequency range of 1 Hz and 1 MHz and the amplitude of 10 mV.

3. Results and discussion

3.1 XRD analysis and cyclic voltammetric study of LaCoO₃

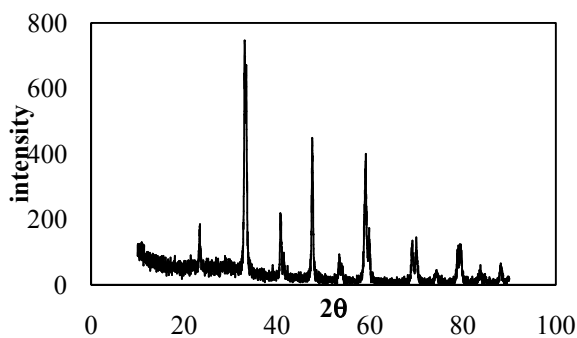


Fig. 1: X-ray diffraction pattern of LaCoO₃

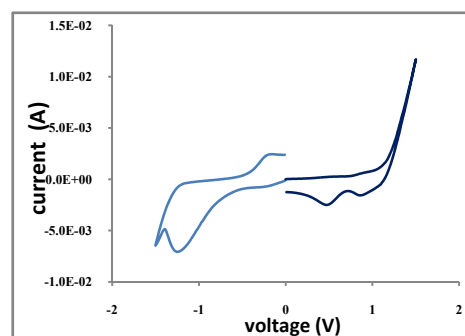


Fig. 2: Cyclic voltammogram of LaCoO₃ in 1M KCl
WE : LaCoO₃/FTO, AE: Pt rod, RE :Ag/AgCl
0 to -1.5V and 0 to 1.5V scan rate of 200 mV/s

The XRD pattern of LaCoO₃ powder at 2θ of 34, 41, 48, 60, 70 and 80 degree, as shown in Fig.1, matched with that from JCPDS (25-1060) LaCoO₃. Fig.2 shows the cyclic voltammogram of LaCoO₃ film without PEO, the reduction peaks at about 0.8 and 0.5 V could correspond to the reduction of Co³⁺ and Co²⁺ respectively which agreed with the result reported by Z. Kebede [9]. Another reduction peak at -1.25 V could due to the hydrogen evaluation reaction.

3.2 Impedance analysis of PEO and PEO/ LaCoO₃

Fig.3a shows the EIS spectra of PEO polymer electrolyte at different applied voltages. The semicircles in high frequency region reflected the properties of polymer electrolyte film, and the oblique lines in low frequency region indicated both the behavior of capacity and the diffusion process and warburg diffusion were observed. The corresponding equivalent circuit is presented in Fig.3b, where R1 is the resistance of cell

besides polymer film. R_p and C_p are the resistance and capacity of polymer electrolyte film. C_d is the interface capacity at the FTO blocking electrodes.

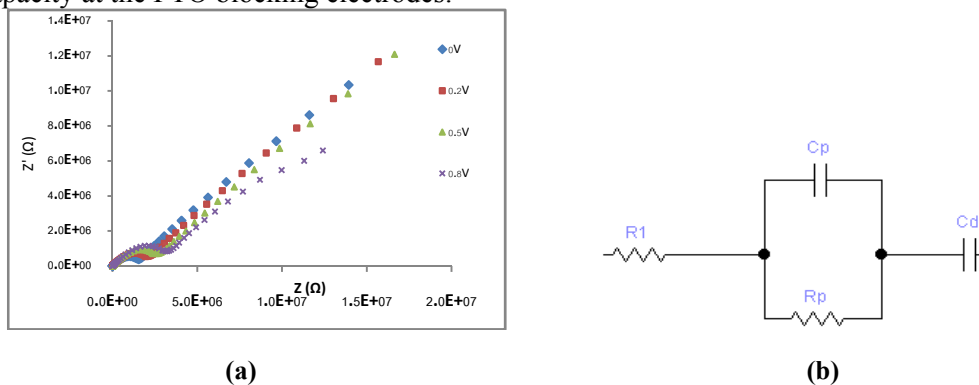


Fig. 3: EIS spectra of PEO electrolyte at different applied voltages (a) equivalent circuit of PEO electrolyte (b)

The value of R_p can be obtained from the diameter of the semicircle. Ion species could diffuse in the PEO matrix. Charge transfer resistance (R_p) of the PEO was in the mega ohm range indicating a low conductivity of PEO electrolyte. The applied voltages showed small change in the charge transfer resistance. However, at 0.8 V the diffusion behavior changed. This might due to the electron transfer incorporated with the charge transfer. When subjected the polymer electrolyte to heat at 60 °C, It was found that the charge transfer resistance decreased reflecting that acetonitrile and ethanol solvent affected the charge transfer behavior of the polymer electrolyte.

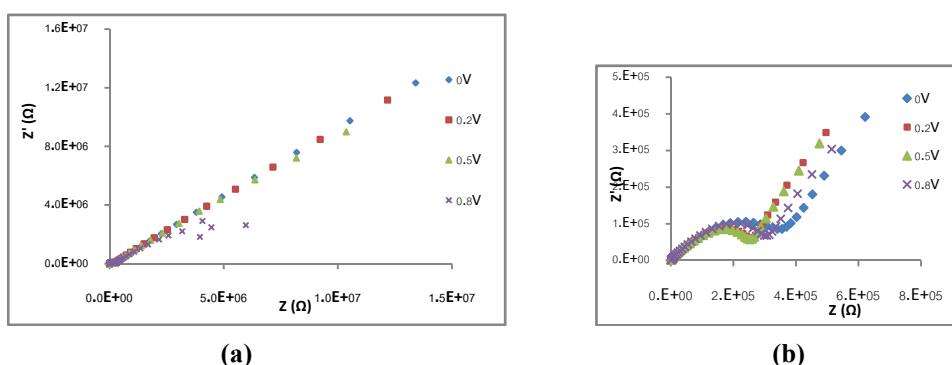


Fig. 4: EIS spectra of PEO electrolyte at different applied voltages, heat at 60 °C (a) and closed up view (b)

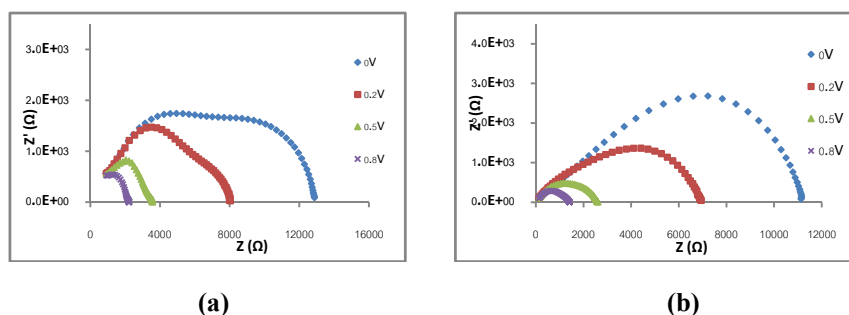


Fig. 5: FTO/PEO-LaCo₃/FTO, Eapp 0 V- 0.8 V (a) after heat at 60 °C (b)

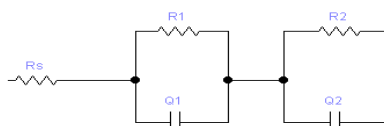


Fig. 6: Equivalent circuit of FTO/PEO / LaCo₃/FTO

EIS spectra of PEO/ LaCoO₃ composite are shown in fig.5 which differed from those of PEO. The two semicircles reflected phase difference of electrolyte composite. The charge transfer resistances given by EIS spectra were due to the bulk and grain boundary resistances of the electrolytes. Charge transfer resistance of the PEO- LaCoO₃ electrolyte reduced from that of PEO about 2 order of magnitude reflecting higher ionic conductivity of PEO/ LaCoO₃. It could be seen that the diameters of semicircles drop fast (lower charge transfer resistance) with the increase of voltage. This might cause by the electron transfer of cobalt species in the composite electrolyte of which depend on the applied potential. When subjected the PEO/ LaCoO₃ solid polymer electrolyte to heat at 60 °C in order to see the effect of the solvent in the electrolyte, It was found that the charge transfer resistance decreased as shown in fig.5(b). The corresponding equivalent circuit of PEO/ LaCoO₃ is presented in Fig.6. The conductivity of polymer electrolyte δ , can be obtained using the following relationship:

$$\delta = L/RA$$

where L is the thickness of the electrolyte and A is the surface area of the film (1.2 cm² and 0.02 cm in this study). The conductivities of the heated PEO/LaCoO₃ polymer electrolytes, calculated at 0, 0.2, 0.5 and 0.8 V were 1.96x10⁻⁶, 3.34x10⁻⁶, 1.21x10⁻⁵, 2.56x10⁻⁵ S/cm respectively.

4. Conclusions

New PEO composite polymer electrolyte using LaCoO₃ as filler was successfully prepared. A substantial enhancement in the conductivity was observed and the charge transfer of PEO/LaCoO₃ polymer electrolyte also depended on the applied potential. The prepared solid polymer electrolyte will be further studied as an electrolyte of metal air battery due to the catalytic activity and oxygen trapping properties.

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6. References

- [1] N. Vassal, E. Salmon, F.Fauvarque, *Electrochim.Acta* . 2000, **45**: 1527
- [2] A. Lewandowski, M. Zajder, D. Frackowiak, F. Beguin, *Electrochim. Acta*. 2001, **46**: 2777.
- [3] D. K. Pradhan, B.K. Sanantaray, R.N.P. Choudhury, A.K. Thakur, *J. Power sources*. 2005, **139**: 384-393.
- [4] K. H. Lee, J.K. Park, W.J. Kim, *J. Polym. Sci. B*. 1999, **37**: 247-252.
- [5] X. Li, Y. Zhao, L.Cheng, M. Yan, X. Zheng, Zi. Gao and Z. Jiang, Enhanced ionic conductivity of poly(ethylene oxide) (PEO) electrolyte by adding mesoporous molecular sieve LiAISBA, *J Solid State Electrochem* 2005, **9**: 609–615.
- [6] T. Itoh, S. Horii, S. Hashimoto, T. Uno, M. Kubo, *Ionics*. 2004, **10** : 450-457.
- [7] T. Kuila, H. Acharya, S.K. Srivastava, B.K. Samantaray and s.Kureti, *Materials Science and Engineering B*. 2007, **137**: 217-224.
- [8] A. Worayingyong, P. Kangvansura and S. Kityakarn, *Colliods and Surfaces A*. 2008, **320**: 123.
- [9] Z. Kebede and S.E. Lindquist, *Sol. Energy Mater. Sol. Cells*. 1998, **51**: 291.