Vol. **129** (2016) *ACTA PHYSICA POLONICA A* No. 4

5th International Science Congress & Exhibition APMAS2015, Lykia, Oludeniz, April 16–19, 2015

Electrical Conductivity, Viscosity and Thermal Properties of TEGDME-Based Composite Electrolytes for Lithium-Air Batteries

M. Kartal*, A. Alp and H. Akbulut
Sakarya University Engineering Faculty, Department of Metallurgical and Materials Engineering,
54187, Sakarya, Turkey

Some important properties of the electrolytes used in Li-air batteries were investigated. Electrolyte composed of a solution of 1 M $LiPF_6$ in tetra ethylene glycol dimethyl ether (TEGDME) was reinforced with SiO_2, Al_2O_3, poly(ethylene) oxide (PEO) and tris (pentafluorophenyl) borane (TPFPB) additives. The effects of these reinforcements on conductivity, viscosity and thermal stability were investigated. Electrical conductivity tests were carried out using a multiparameter meter. Viscosity tests were performed in a viscometer using tuning-fork vibration method. Thermal stability of the electrolytes was tested by both TG and DSC.

DOI: 10.12693/APhysPolA.129.816

PACS/topics: 88.80.F–, 88.80.ff, 82.45.Gj, 82.45.Wx, 81.07.–b

1. Introduction

Energy density development is required to satisfy the energy storage needs of society in long term. Due to its high theoretical specific energy, lithium-air battery system is an extremely attractive technology for electrical energy storage that could make long-range electric vehicles widely affordable. Lithium-air batteries have ultra-high theoretical specific energies of 11 $\mathrm{kWh\,kg^{-1}}$ based on the lithium electrode alone or about 5.2 $\mathrm{kWh\,kg^{-1}}$ when the oxygen weight is included, which is almost 10 times that of the state-of-the-art Li-ion battery technology [1, 2]. However, in practical sense, there are significant barriers still to be overcome before the practical application of rechargeable Li-air batteries will become possible. Dendrite formation of Li metal anode and its high reactivity with air still remain challenges to overcome [3]. It is well known that the reduced oxygen species are generated on the cathode-electrolyte interface during the discharge process of the Li-air battery [4, 5]. These species are chemically reactive and may cause decomposition of all battery components; electrolyte (solvent, salt and additives), cathode supporting materials (substrate; typically carbon, binder and current collector), and even separator [6]. The insulating products of decomposition are formed on the cathode and cause a rapid capacity fading.

The electrolyte has a key role in non-aqueous lithium-air batteries because of its fundamental importance in producing the appropriate reversible electrochemical reduction. Tetra ethylene glycol dimethyl ether (TEGDME) is known by its higher specific capacity as compared to carbonates and other ethers. Moreover, it is more stable to formation of Li_2O_2 in the first cycles. TEGDME is a polar versatile solvent which displays a high $LiPF_6$ solubility to produce well-conducting solutions with a wide electrochemical window [7].

Several studies have been reported to add ceramic nano fillers to aprotic solvents especially the polymer electrolytes for lithium batteries. By this approach, it was found that there is an increase in conductivity and mechanical strength [8]. It is also noteworthy that adding PEO just as ceramic nano powders would form a solid electrolyte interface to protect lithium metal anode.

The insoluble solid reaction products in the organic electrolytes are accumulated within the pores of the air electrode and impede the rechargeability of Li-air batteries. To avoid the precipitation of reaction products and the passivation of the electrode surface, appropriate polar solvents are required to dissolve these solid products. Importantly, it was reported that TPFPB can partially dissolve insoluble lithium-oxygen products formed at the air cathode and thereby a more active carbon surface can be exposed for further oxygen reduction reaction (ORR) during the discharge process [9].

In this study, SiO_2, Al_2O_3, PEO and TPFPB were added to electrolyte composed of 1 M of $LiPF_6$ in TEGDME. The properties of pristine and composite electrolytes were investigated and characterized by using a multiparameter meter, a viscometer and a thermal analysis instrument.

2. Experimental details

Anhydrous TEGDME was purchased from Alfa Aesar and treated with molecular sieves to remove the impurities prior to use as the electrolyte. A solution of 1 M $LiPF_6$ (Aldrich) in tetra(ethylene glycol) dimethyl ether (tetraglyme, Aldrich) was used as the electrolyte. Lithium hexafluorophosphate ($LiPF_6$) ($>$ 98.0%) was

---

*corresponding author; e-mail: kartal@sakarya.edu.tr dried at 50 °C for 3 hours under argon atmosphere. Al_2O_3 (> 99.99%, < 50 nm) and SiO_2 (> 99.99%, < 80 nm) were also dried at 100 °C for 72 hours to remove humidity. PEO and TPFPB were also dried with molecular sieves. 1 M $LiPF_6$ in TEGDME electrolyte was prepared and the amount of 0.1 wt.% Al_2O_3, 0.1 wt.% SiO_2, 1% PEO and 4% (0.1 M) TPFPB were added to solvent and mixed vigorously by magnetic stirring and stored in amber glass sample vials in an MBraun dry box filled with purified argon. The moisture and oxygen content were less than 1 ppm.

Conductivity tests were carried out by using Eutech Instruments PCD 650 Multiparameter meter at room temperature under argon atmosphere. The viscosity tests were made using AAND SV-10 Viscometer at room temperature under air atmosphere. Thermal characterization of electrolytes by TG/DSC was performed on a NETZSCH STA 449 F1 with heating rate of 10 °C min^{-1} in nitrogen atmosphere. The masses of the samples were around 20 mg, flow rate was 40 ml min^{-1} and the measurement temperature range was from 25 °C to 400 °C.

3. Results and discussion

Table I shows the viscosity and the conductivity values of the electrolytes. Predictably, addition of Al_2O_3 and SiO_2 nano powders resulted in a slight increase in the viscosity while the conductivity of the nanocomposite electrolytes slightly decreased as compared to the base electrolyte with the same $LiPF_6$ content. Finer-particle-sized Al_2O_3 nano-powder-reinforced electrolyte had an increased viscosity but showed a slightly higher conductivity compared to those of SiO_2 [10]. PEO-reinforced electrolyte showed the highest viscosity and a lower conductivity. As compared to the electrolytes with nano ceramic powders, TPFPB-reinforced electrolyte had a higher viscosity and a lower conductivity. Low conductivity value can be attributed to large molecule formation of TPFPB (Lewis interaction) [11].

TABLE I

Conductiviy and viscosity values of the electrolytes.

No.	Electrolytes	Additives	Conductiviy [mS/cm]	Viscosity [mPa s]
1	1M $LiPF_6$/TEGDME	–	2.386	14.65
2	1M $LiPF_6$/TEGDME	%0.1 Al_2O_3	2.378	16.28
3	1M $LiPF_6$/TEGDME	%0.1 SiO_2	2.370	15.80
4	1M $LiPF_6$/TEGDME	%1 PEO	1.974	24.52
5	1M $LiPF_6$/TEGDME	0.1 M (%4) TPFPB	2.151	15.68

Figure 1 illustrates TG and DSC curves of pristine electrolyte composed of 1 M $LiPF_6$ in TEGDME. Evaporation of solvent (TEGDME) starts at 160 °C and finishes at 221 °C. The last compound in the sample carrier is LiF originated from $LiPF_6$ salt. Endothermic peaks are observed at 97 °C, 221 °C and 242 °C on DSC curves. Decomposition reaction peak of $LiPF_6$ generally occurs at temperatures between 63 °C and 78 °C. However, in our study it was detected approximately at 97 °C [12, 13]. $LiPF_6$ and TEGDME have evaporated at 221 °C. Small endothermic peak at 242 °C could be attributed to melting of Li salts (LiF) [14].

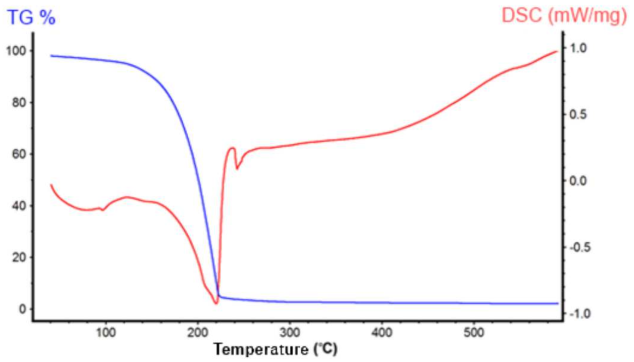

Fig. 1. DSC and TG curves of pristine electrolyte (1 M $LiPF_6$ in TEGDME).

To determine thermal stabilities of the electrolytes TG tests were carried out and the results are illustrated in Fig. 2. As can be seen in Fig. 2, all additives except TPFPB have increased the weight loss temperatures. However, no significant effect on the thermal stability was observed when the additives were used. When TPFPB was added into the base electrolyte (1 M $LiPF_6$ in TEGDME) the weight loss had occurred at relatively lower temperatures.

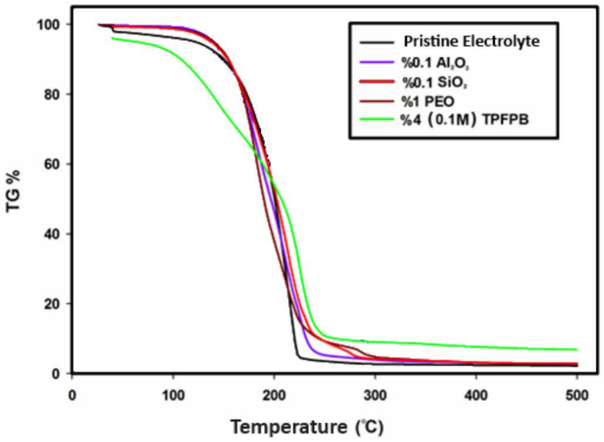

Fig. 2. TG curves of the electrolytes.

4. Conclusions

Composite electrolytes were produced from 1 M $LiPF_6$ in TEGDME with SiO_2, Al_2O_3, PEO and TPFPB prepared using magnetic stirring. The main conclusions of the investigation are as follows: The conductivity of the electrolytes was decreased and the viscosity of the electrolytes was increased with the addition of such additives. PEO has shown the most significant effect on the viscosity and the conductivity properties. DSC and TG analyses of the pristine electrolyte where performed. Thermal stabilities of the composite electrolytes were also studied. Results have shown that the additives (except TPFPB) slightly increased the thermal stability of pristine electrolyte.

Acknowledgments

This research has received funding from the Seventh Framework Programme FP7/2007-2013 (Project STABLE – Stable high-capacity lithium-Air Batteries with Long cycle life for Electric cars) under grant agreement 314508.

References

[1] L.J. Hardwick, P.G. Bruce, *Curr. Opin. Solid St. M.* **16**, 178 (2012).

[2] W. Xu, J. Hu, M.H. Engehard, S.A. Towne, J.S. Hardy, J. Xiao, J. Feng, M.Y. Hu, J. Zhang, F. Ding, M.E. Gross, J.G. Zhang, *J. Pow. Sourc.* **215**, 240 (2012).

[3] F. Mizuno, K. Takechi, S. Higashi, T. Shiga, T. Shiotsuki, N. Takazawa, Y. Sakurabayashi, S. Okazaki, I. Nitta, T. Kodama, H. Nakamoto, H. Nishikoori, S. Nakanishi, Y. Kotani, H. Iba, *J. Pow. Sourc.* **228**, 47 (2013).

[4] C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, M.A. Hendrickson, *J. Phys. Chem. C* **113**, 20127 (2009).

[5] B.D. McCloskey, R. Scheffler, A. Speidel, G. Girishkumar, A.C. Luntz, *J. Phys. Chem. C* **116**, 23897 (2012).

[6] E. Nasybulin, W. Xu, M.H. Engelhard, Z. Nie, X.S. Li, J.G. Zhang, *J. Pow. Sourc.* **243**, 899 (2013).

[7] C.Ó Laoire, S. Mukerjee, E.J. Plichta, M.A. Hendrickson, K.M. Abraham, *J. Electrochem. Soc.* **158**, A302 (2011).

[8] H. Tokuda, M. Watanabe, *Electrochim. Acta* **48**, 2085 (2003).

[9] N. Choi, G. Jeong, B. Koo, Y. Lee, K.T. Lee, *J. Pow. Sourc.* **225**, 95 (2013).

[10] D. Sharma, A. Mukherjee, *Int. J. En. Technol. Adva. Eng.* **4**, 60 (2014).

[11] J.E. Seo, M.Sc. Thesis, Korea Advanced Institute of Science and Technology, 2006.

[12] L.S. You, M.P. Hua, C.X. Ling, R.Q. Du, L.F. Qiang, *J. Chem. Sci.* **120**, 289 (2008).

[13] D. Lee, J. Hassoun, S. Panero, Y.K. Sun, B. Scrosati, *Electrochem. Commun.* **14**, 43 (2012).

[14] E. Zinigrad, L.L. Asraf, J.S. Gnanaraj, M. Sprecher, D. Aurbach, *Thermochim. Acta* **438**, 184 (2005).