The Effect of Inorganic Nano Powder Additives in TEGDME for Lithium Air Batteries

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SiO_2 and Al_2O_3 nano fillers were added to an electrolyte composed of a solution 1 M $LiPF_6$ in tetra ethylene glycol dimethyl ether (TEGDME) and the effects of these nano powders on capacity and cycling performances were investigated. Galvanostatic charge/discharge (GC) measurements were performed in the assembled Li-air cells by using the nanocomposite electrolytes. The discharge capacities of these cells were cyclically tested by a battery tester at a constant current in the voltage range between 2.15 V and 4.25 V. Discharge products of nanocomposite electrolytes were characterized by SEM and XRD spectroscopies. The electrochemical results demonstrated that Al_2O_3 reinforced electrolyte showed higher discharge capacity and cyclability than those of SiO_2 reinforced electrolyte.

Introduction

A breakthrough in energy density is required to satisfy the energy storage needs of society in the 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 kWh kg^{-1}, if based on the lithium electrode alone, or about 5.2 kWh kg^{-1}, when the oxygen weight is included, 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 have to be overcome before the practical application of rechargeable Li-air batteries is possible. Dendrite formation of Li metal anode and its high reactivity with air still remain the 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]. Therefore, insulative decomposed products are formed on a 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 the other ethers; moreover, it is more stable to form Li_2O_2 in the first cycles. However, it has a low cycling performance [7].

Several studies has been reported to add ceramic nano fillers to aprotic solvents, especially polymer electrolytes for lithium batteries. By this approach, it is found that there was an increase in conductivity and mechanical strength [8].

In this study, SiO_2 and Al_2O_3 nano fillers are added to an electrolyte composed of a solution of $LiPF_6$ in TEGDME. A lithium foil was used as an anode material and a gas diffusion layer (GDL) was used as a cathode material. 1 M of $LiPF_6$ and TEGDME electrolyte has been produced and amount of 0.1 wt.% Al_2O_3 and SiO_2 were added to this solution in order to compare the effects on efficiency of the Li-air cells. The effects on capacity and cycling performances and the properties of the as-produced electrolytes were investigated and characterized by using XRD and SEM spectroscopies. The electrochemical properties of the electrolytes were also tested in order to evaluate the battery performance.

2. Experimental details

2.1. Cell assembly

The gas diffusion layers (GDLs) (SIGRACET 24BC, SGL Carbon Inc.) with an area of 2.54 cm^2 were dried overnight at 55 °C. Anhydrous TEGDME was purchased from Alfa Aesar and treated with molecular sieves to remove the impurities prior to use as the electrolyte. A lithium foil disk was used as an anode material and a gas diffusion layer (GDL) was used as a cathode material, while glass fiber (18×0.65 mm, ECC1-01-0012-A/L) saturated in the electrolyte was used as a separator. 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 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. 1 M $LiPF_6$ in TEGDME electrolyte was prepared and ratio of 0.1 wt.% Al_2O_3 and 0.1 wt.% SiO_2 added to solvent and mixed vigorously by magnetic stirring and stored in amber glass sample vials

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in an MBraun dry box filled with purified argon. The moisture and oxygen content were less than 1 ppm.

The Li-air cell was then assembled in an Ar-filled dry glove box (MBraun LABstar) using an ECC-Air electrochemical cell (EL-Cell, GmbH) configuration with openings allowing oxygen to inlet and outlet through the cathodic side.

2.2. Characterizations of electrolytes

Conductivity tests were carried out by using Eutech Instruments PCD 650 Multiparameter at room temperature under argon atmosphere and viscosity tests were applied by AAND SV-10 Viscometer at room temperature under air atmosphere. The morphology of the discharge products on cathode was observed by scanning electron microscopy (SEM) (JSM-6060 LV system). Surface characterization of the discharged cathode was also investigated by X-ray diffraction (XRD) (Rigaku D/MAX 2000). The cells were cyclically tested on a MTI Model BST8-MA electrochemical analyzer using 0.10 mA/cm^2 current density over a voltage range of 2.15–4.25 V and the oxygen gas flow rate was 15 ml/sec. All electrochemical measurements were carried out at room temperature (25 °C).

3. Result and discussion

Figure 1a and 1b show the viscosity and the conductivity of the electrolytes. Predictably, addition of Al_2O_3 and SiO_2 nano powder 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 has increased the viscosity but showed a slightly higher conductivity than that of SiO_2 [9].
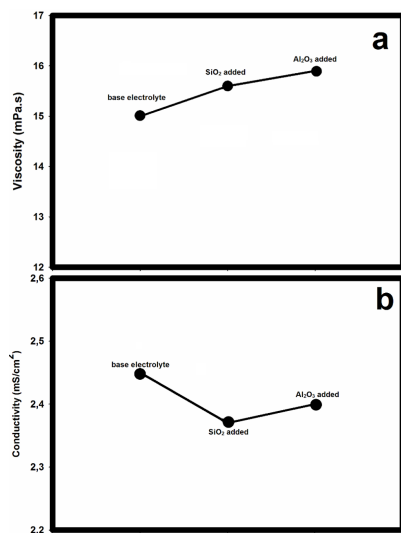

Fig. 1. The influences of the nano fillers on a) viscosity, b) conductivity.

Figure 2 shows the cathode surfaces of the nanocomposite electrolytes after 10 cycles. It is found that both nano fillers have accumulated on the surface with the discharge products and thus have occluded the pores. It is
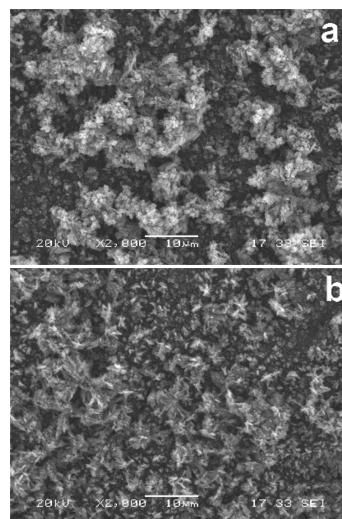

Fig. 2. SEM images of the cathodes working with electrolytes including a) 0.1 wt% SiO_2, b) 0.1 wt% Al_2O_3.

also obvious that SiO_2 powders are more prone to accumulation on the cathode surface with aggregation. This is because of particle size of the powders. Al_2O_3 nano fillers are randomly dispersed in the microstructure and do not exhibit the coarsened microstructure of SiO_2 powders.

X-ray diffraction patterns of the two different electrolytes are shown in Fig. 3. The typical reflection peak of carbon is observed. SiO_2 and Al_2O_3 peaks are also appeared with the discharge products; Li_2CO_3 is the predominant and Li_2O_2, LiO_2 are the by-products.
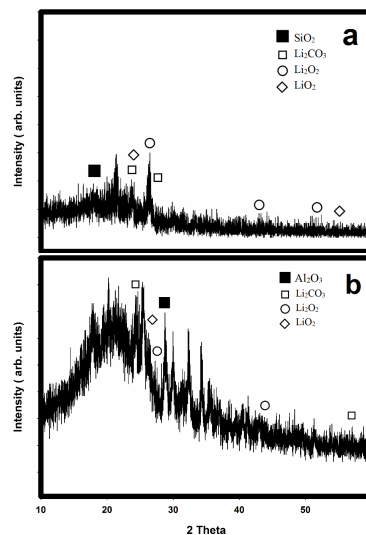

Fig. 3. XRD peaks of the electrolytes including a) 0.1 wt% SiO_2, b) 0.1 wt% Al_2O_3.

Figure 4 displays the performance at first three cycles of the nanocomposite electrolytes, produced with addition of two different nano fillers, at a current density of 0.10 mA/cm^2 and potential between 2.15 and 4.25 V. As shown in Fig. 4b, the electrolyte containing 0.1 wt.% Al_2O_3 exhibited approximately two times higher capac-
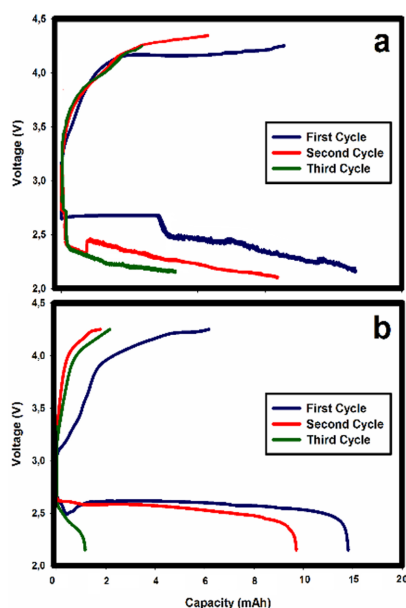
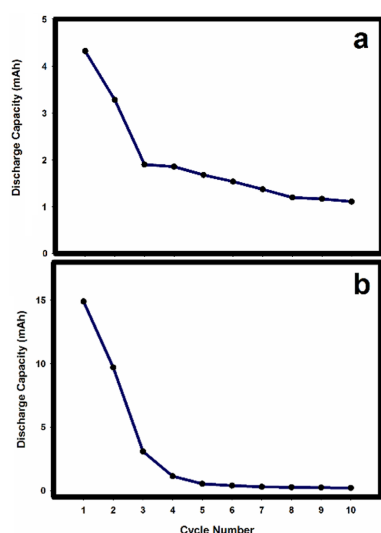Fig. 4. The first three cycles of the electrolytes including; a) 0.1 wt% SiO_2, b) 0.1 wt% Al_2O_3.

Fig. 5. The effects of the nano fillers on cycle performance a) 0.1 wt% SiO_2, b) 0.1 wt% Al_2O_3.

ities than 0.1 wt.% SiO_2 at the first two cycles, but the capacities have rapidly decreased at the third cycle. This can be related to occlusion of cathode pores with correspondingly finer particle-sized Al_2O_3 and also with the decomposition of the solvent [10]. As demonstrated in Fig. 4a, SiO_2-reinforced electrolyte demonstrated relatively better coulombic efficiency and stability than Al_2O_3-reinforced electrolyte, but quite lower capacities were obtained at the first two cycles.

Figure 5 shows the ten-cycle-performances of the nanocomposite electrolytes containing two different nano fillers at a current density of 0.10 mA/cm^2 and potential between 2.15 and 4.25 V. SiO_2 added electrolyte showed higher stability but lower initial capacities than

Al_2O_3 added electrolyte. Since the discharge products and SiO_2 particles, substantially deposited on the cathode surface, formed amorphous and porous layer, a limited cathode surface area is observed. This resulted in a relatively lower capacity performance but higher cyclic performance than in Al_2O_3-added electrolyte [11]. Depending on the pore sizes of the cathode, finer Al_2O_3 particles were well dispersed on the surface, but have penetrated into the pores and hindered the oxygen transfer into the lithium air cell, which resulted in 0.472 mAh at 10th cycle, while the SiO_2-added electrolyte showed 1.266 mAh at the same cycle.

4. Conclusions

Nanocomposite electrolytes were produced from 1 M $LiPF_6$ in TEGDME with SiO_2, Al_2O_3 additives, and prepared by using magnetic stirring. The main conclusions of the investigation are as follows: The surface morphology of the cathode was affected by inorganic additives, and relatively higher discharge capacities were obtained at the first two cycles in Al_2O_3-added electrolyte. However SiO_2 demonstrated more stable charge/discharge characteristic than that of Al_2O_3-added nanocomposite electrolyte. Respectively a high reversible capacity, and fairly good cyclability was achieved for 1 M $LiPF_6$ in TEGDME with 0.1 wt.% SiO_2 addition.

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