Four discharge plateaus of Lithium/Sulfur secondary battery with $(PEO)_6LiBF_4$-Al_2O_3 composite polymer electrolyte prepared by ballmilling

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A battery based on the Lithium/Sulfur redox couple has a theoretical specific capacity of 1672mAh/g of active material and a specific energy of 2600Wh/kg, assuming complete reaction to the product Li_2S. Therefore, there is a strong incentive to develop Li/S batteries.

The linear PEO-LiX polymer electrolytes generally have some problems for lithium polymer rechargeable batteries such as poor mechanical property, low ionic conductivity at low temperature, and reactivity of lithium metal anode.

Recently, Many research efforts to overcome the problems have been directed towards the use of nano-scale ceramic filler such as Al_2O_3, SiO_2, and TiO_2 in PEO based polymer electrolyte.

We had reported that the PEO and PVdF-based polymer electrolyte prepared by ball milling for lithium/sulfur battery show the higher ionic conductivity and the good interfacial stability.[1,2] Among them, PEO-$LiBF_4$ polymer electrolyte prepared by ball milling for 12h showed the discharge plateau according to polysulfide, Li_2Sn, at high voltage ranging from 2.6V to 2.2V

In this study, we have introduced nano-sized Al_2O_3 on ball milling in order to investigate the discharge process of PEO-$LiBF_4$ polymer electrolyte prepared by ball milling for lithium/sulfur battery.

Experimental procedures

Polymer electrolytes were prepared by ball milling from a mixture of PEO(Aldirch, Mw = 4,000,000), Al_2O_3(Aldrich, nano-size) as ceramic filler, and $LiBF_4$ as Li salt in acetonitrile. Discharge characteristics of Li/$(PEO)_6LiBF_4$-Al_2O_3/ 50wt.%Sulfur cell were investigated using a Swagelok cell. Lithium/sulfur cells were assembled in a glove box filled with argon gas.

Cell performance was measured with cut-off voltage of 1.5~3.4V vs. Li/Li^+. To characterize discharge process of lithium/sulfur cell and analyze the intermediates of lithium/sulfur reaction, linear sweep voltammetry and UV-VIS spectroscopy were carried out using EG&G 263A and Lambda 900.

Results

Sulfur electrode forms the lithium polysulfide such as Li_2S_4, Li_2S_6, Li_2S_8 etc. before complete reaction to Li_2S. Up to date, it has been reported two discharge plateau according to 2.4 and 2.0V(vs Li/Li+) for Li/S battery with various kinds of polymer electrolyte.[3] In this study, the discharge behavior showed four discharge plateau at about 2.6, 2.4, 2.2, and 2.0 voltage in accordance with Li_2Sn(n=2, 4, 8), and moreover, $(PEO)_6LiBF_4$-Al_2O_3 composite polymer electrolyte had the definite four discharge plateau compared with without it.

In order to investigate the reductant corresponded to each discharge plateau during discharge of sulfur electrode, absorbance spectra of the soluble polysulfide formed in the cathode were monitored by UV spectrometer.

The peaks in accordance with the formation of the polysulfide such as S_8^{2-}, S_4^{2-}, S_2^{2-} were detected at each discharge plateau region by investigation of UV-VIS spectra.

References

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Fig. 1. Linear sweep of the Li/CPE/Sulfur cells with scan rate of $0.01mVs^{-1}$ at 80℃

Fig. 2. Discharge profile of Li/CPE/S cell with discharge current rate of $0.07mA/cm^2$ at 80℃