Fabrication of Lithium Nitride Film as a Protective Layer for the Li-S Secondary Battery System

Jong-Ki Lee[a], , Yun-Seok Choi[b]
[a] Mobile Energy Business Team, Samsung SDI Co. Ltd., Chonan, Korea
[b] Energy Development Team, CRD Center, Samsung SDI Co. Ltd., Yongin, Korea

Chung-Kun Cho, Sang Mock Lee
MD Lab, Samsung Advanced Institute of Technology, Suwon, Korea

The use of lithium metal as an anode material can be the most promising way to develop an attractive battery system with a high energy density. It is based on the fact that the Li is the lightest metal and has the lowest redox potential out of all emf series. However, the dendrite growth of the Li metal during charge (Li deposition) and the local selective dissolution of the Li dendrites during discharge reaction is the main problem in realization of Li metal anode, which lowers the Li cycling efficiency.

One of the possible methods to increase the Li cycling efficiency is to form a PL(s) (protective layer) on the Li anode surface. The major roles of a PL(s) are to prevent the dendrite growth physically and to isolate the Li metal surface from the liquid electrolyte. Therefore, the electrochemical properties of PL should satisfy following requirements basically, (1) high Li ionic conductivity, (2) dense microstructure, and (3) chemical stability with Li. One of candidates is Li_3N because its Li ion conductivity is about 10^{-3} S/cm order of magnitude and it dose not react with Li.

The nitration of Li can be achieved simply by introducing pure N_2 gas into the fresh Li surface, for example the vacuum deposited Li, even at the room temperature and in the lower pressure than the atmosphere. However, very intensive gas reaction and low temperature synthesis made its microstructure porous and poor crystalline, respectively. Fig. 1 shows the SEM photograph of the nitrated Li surface by simple gas reaction. The average pore size is about 0.3 ~ 0.5 ㎛ and the ratio of Li to N is 5 according to the XPS analysis. Fig. 2 shows an X-ray diffraction pattern for the nitrated sample. As shown in Fig. 2, the only peaks of PP (Polypropylene) from cover film on the sample could be found. These microstructural properties could not be improved by annealing the sample at elevated temperature for 1 hr and we could not raise the annealing temperature due to the low melting point of Li (180 ℃).

In general, the IBAD (Ion Beam Assisted Deposition) is a well-known process for preparing the crystalline thin film *in situ* during vacuum deposition so that this method using low energy nitrogen ion gun is expected to be very effective on fabricating the crystalline lithium nitride. Now we are trying to deposit the Li_3N crystalline film *in situ* using the hollow cathode plasma floated by acceleration potential and the analysis on the basic data related to the microstructure and the electrochemical property is preceded. The performances as a protective layer for the Li metal electrode will be compared according to the microstructural variations that depend on the nitration method, in future works.

REFERENCES

1. M. F. Bell, U. v. Alpen, *J. Electroanal. Chem.*, **129** (1981) 315-319.
2. Duncan H. Gregory, *Coordination Chemistry Reviews*, **215** (2001) 301-345.
3. Yongzhong Jia, Jinxian Yang, *Solid State Ionics*, **96** (1997) 113-117.
4. C. Brissot, M. Rosso, J-N. Chazalviel, S. Lascaud, *J. Power Sources*, **81-82** (1999) 925-929.
5. Toshiyuki Hayashi, Akihito Matsumuro, mutsuo Muramatsu, Masao Kohzaki, Katsumi Yamaguchi, *Thin Solid Film*, **376** (2000) 152-158.

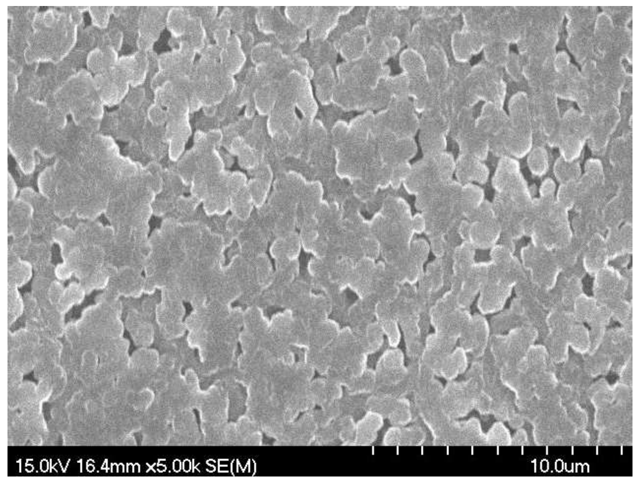

Fig. 1 SEM photograph of nitrated sample fabricated by simple gas reaction

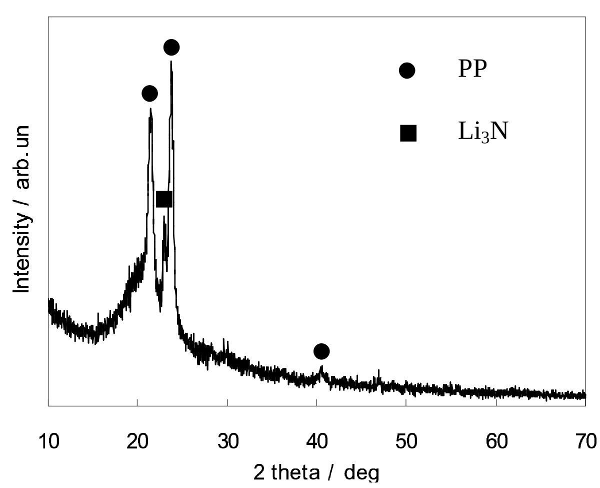

Fig. 2 XRD pattern of nitrated sample fabricated by simple gas reaction. The PP film is used to protect the sample from air.