THE RAMAN STUDY OF SEI FILM OF ANODE MATERIAL IN LITHIUM ION BATTERIES

Hua Dong[1], Zhaoxiang Wang[2], Ying Bai[1], Yujun Mo[1]*, Xuejie Huang[2], Liquan, Chen[2]

[1]Physics Department, Henan University, Kaifeng 475001, China; E-Mail: yujunmo@henu.edu.cn
[2] Institute of Physics, Chinese Academy of Sciences, 100080, China

Keywords: *Lithium Ion Batteries, Solid Electrolyte Interface; HCS, SERS*

Abstract: Surface Enhanced Raman Scattering (SERS) was employed to study the Solid Electrolyte Interface (SEI) film in lithium ion batteries in this work. Silver island film was deposited on the surface of Hard Carbon Spherule (HCS) and this resulted in SERS effect and the SEI film discharged to different voltages was analyzed and its Raman spectra were assigned.

The breakthrough of the technology of the anode materials of batteries has lead to the birth and commercialization of lithium ion batteries since the late twentieth century and from then on the anode materials have always been the hotspot in this area. While studying the way to enhance the cycling capability and capacity of batteries, many researchers reported the Solid Electrolyte Interface (SEI) film between the electrode and electrolyte [1-2]. This film is an insulator for electron and a good conductor for lithium ion which can freely insert and deinsert through this passivate film. The formation of this film has a crucial influence upon the capability of electrode materials [3]. The study of SEI film has been a focus in the area of lithium ion batteries in recent years.

Silver particles were chemically deposited on the surface of HCS particles, which is a kind of cathode material for lithium ion batteries. Silver island film deposited upon can result in SERS effect through comparing the Raman spectra of HCS powder before and after silver particles were deposited. Then we assembled a series of experimental batteries in which HCS (without binder or black carbon) was cathode material with silver island film deposited on its surface lithium metal (purity 99.99%) as anode material, polypropylene micropore membrane (Cellgard 2300) as cellgard for electrode, and nonaqueous electrolyte system 1M $LiPF_6$ EC/DMC (1:1/V:V) was employed. The well-assembled batteries were discharged and recharged to different voltages and the Raman spectra of SEI film were analyzed and assigned.

The Raman signals were gathered by a Renishaw RM-1000 Micro Raman spectroscopy with 514.5nm line from an argon ion laser as excitation. Fig 1. shows the Raman spectra of the SEI film discharged to different voltages in the experimental batteries, which were assembled with HCS as its active material with silver island film deposited on it. As the characteristic vibrational mode of electrolyte solvent DMC (CH_3 distortion vibration) lies at 518cm^{-1} [4], and that of EC lies at 895cm^{-1} (ring-breath vibration) and 715cm^{-1} (ring-bend vibration) [4]. The characteristic vibrational mode of DMC at 518cm^{-1} can't be seen in the figure, which account for the volatilization of DMC for it's easy to volatilize. While the characteristic vibrational modes of EC 895 cm^{-1} and 715cm^{-1} are apparent which results from the volatilization difficulty of EC. As the above discussion is concerned, we should take the influence of EC and $LiPF_6$ into account, so in the figure the Raman Spectra of electrolyte 1M $LiPF_6$ EC/DMC was offered as reference in Fig. 1. The two characteristic

Raman peaks of carbon material are apparent in the figure. The mode 1360cm^{-1} can be assigned to D-band, which corresponds to typical amophous carbon, and irregular graphite while 1590cm^{-1} can be assigned to G-band [5]. We can see from Fig. 1. that the positions of the Raman peaks and the relative intensity of the peaks are changed with different discharged voltage. Detailed analyses of the results demonstrate that the species and content of the resultant discharged to different voltages are different, and the species and each content of them in SEI film have relation to the voltages discharged and recharged, which is a dynamic process.

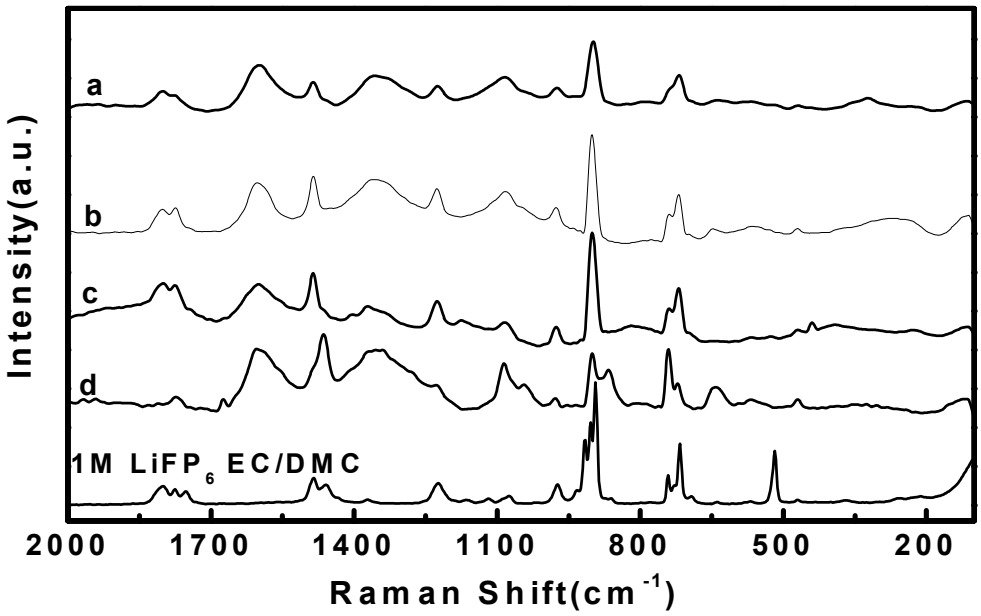

Fig 1. The Raman Spectra of electrodes discharged to different voltages with HCS as working electrode assembled to experimental batteries after silver island film was deposited on the surface (a) discharged to 1.0V; (b) to 0.7V; (c) to 0.5V; (d) to 0V.

Acknowledgements:
This work was supported by Chinese National Nature Foundation (No. 10274019) and Nature Foundation of Henan province (No.0211010100)

References:

1. Z.X. Shu, R. S. McMillan, J. J. Murray, J. Electrochem. Soc. **140**, 922 (1993).
2. H. Ota, A. Kominato, W. Chun, et al. Extended abstract No. 201, 11th International Meeting on Lithium Batteries, Monterey, California, (2002).
3. J. M. Tarascon, M. Armand, Nature, **414,** 359 (2001).
4. T. Eriksson, A. M. Andersson, A. G. Bishop, et al. J. Electrochem. Soc. **149**, A69 (2002).
5. M. S. Dresselhaus, G. Dressselhaus, M. A. Pimenta, et al. Ox- Blackwell Science, **367**, 1999.