2B04

SFG 分光法による炭素−電解質溶液界面の構造研究

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The Study on Carbon Electrode/Electrolyte Interface by Sum Frequency Generation

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１.【目的】As an important rechargeable battery, Li-ion battery is widely used in portable electric devices due to its high capacity and output voltage.[1] Typically, mixed cyclic carbonates and linear carbonates with Li-salt are used as electrolyte solutions for the commercial available Li-ion batteries. It is essential to understand the structures at the electrode/electrolyte interface where the charging / discharging reactions occur and can significantly affect the reversibility and the capacity fading cycling of the Li-ion batteries. As a 2nd-order nonlinear optical technique, sum frequency generation (SFG) vibrational spectroscopy (Fig. 1) is a powerful tool and highly sensitive to the surface and interface. In our previous studies, the adsorption structure of the solvents on the $LiCoO_2$ surface, which is one of most common cathode for Li-ion battery, has been systematically investigated by SFG spectroscopy.[2, 3]

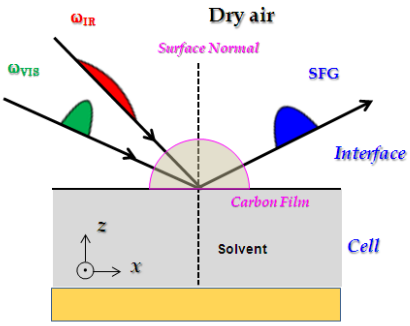

Fig.1. Diagram of Sum Frequency Generation

In the present study, the adsorption of the carbonate solvents on the carbon electrode, a typical anode material for Li-ion battery, has been investigated by *in situ* SFG spectroscopy for the first time. The structual information of solvent adsorption on the carbon electrode surface is important to understand the formation process of solid electrolyte interface (SEI) on the anode surface, which can significantly affect the stability and durability of Li-ion battery.

２.【実験】A broadband SFG system with a tunable femtosecond infrared pulse and a picosecond visible pulse at 800 nm was employed to investigate the molecular structure on the carbon thin-film surface.[2,3] The *in-situ* SFG observation was carried out in the frequency region of 1400 ~ 2200 cm^{-1}, under *ssp*- and *sps*-poalrization combiantions. Usually, SFG spectra were normalized by an SFG spectrum of a evaporated gold film on the same substarate surface. SFG spectral intensity can be described as

$$I \propto \left| \sum_q \frac{A_q}{\omega_{IR}-\omega_{v,q}+i\Gamma_q} e^{i\varepsilon} + \chi_{NR}^{(2)} \right|^2 \qquad (1)$$

where, A_q, $\omega_{v,q}$ and Γ_q are the amplitude, resonant frequency, and damping coefficient of q^{th} vibrational mode, respectively. $\chi_{NR}^{(2)}$ is the second-order non-resonant susceptibility. The carbon electrode was thermally evaparated onto the surface of a pre-cleaned CaF_2 substrate in the vacuum chamber (~1 Pa). The thikness of the carbon thin-film electrode was ca. 40 nm. Raman spectroscopy and atomic force mircoscope were used to evaluate the degree of the graphitization and the mophorlogy of the carbon thin-film, respectively. The carbon electrode was assembed onto an electrochemical SFG cell. Li foils were used as counter and reference electrodes. Two commercial carbonate solvents of propylene carbonate (PC) and dimethyl carbonate (DMC) containing 0.1M $LiClO_4$ or $LiPF_6$ were used as supporting electrolyte solution in this work.

３.【結果と考察】First, the basic spectroscopic behaviors of bulk solvents were investigated by Raman and IR spectroscopy. Figure 2 shows (a) IR and (b) Raman spectra of pure PC solvent frequency region of 1700~1900 cm^{-1}. One sharp peak around 1780 cm^{-1} can be observed in both Raman and IR spectra which can be ascribed to the C–O stretching mode of carbonyl group of the PC molecules in bulk. Based on the selection rule for the SFG spectroscopy, the active SFG vibrational mode should have activity in both Raman and IR spectra.

In order to distinguish the structural difference between the bulk and interface, the SFG spectra of PC solvent were recorded at the air/liquid interface which will help us to further understand the structure on the carbon surface in electrolyte solution. Figure 2c shows an SFG spectrum of PC at air/liquid interface with *ssp*-polarization (blue trace is experimental result while red trace is a fitting result based on Eq. 1). The SFG spectrum at PC/air interface with a reasonable spectral intensity indicates that PC molecules should take some ordered arrangement on the liquid/air interface since random surface structure will not give any contribution to the SFG signals. Two vibrational modes (green trace in Fig. 2c) can be distinguished by the fitting processes (Eq.1). One is located at 1781 cm^{-1}, close to that obtained by Raman and IR spectroscopic measurement (Figs. 2a and 2b). Another peak is observed at 1814 cm^{-1}. The latter peak shows much higher spectral intensity with a blue shift of approximately 33 cm^{-1} in contrast with the former one. The peak observed at higher frequency is definitely attributed to the molecules organized at the liquid/air interface. The both vibrational modes can be attributed to C=O stretching mode of PC molecules on the liquid surface.[4]

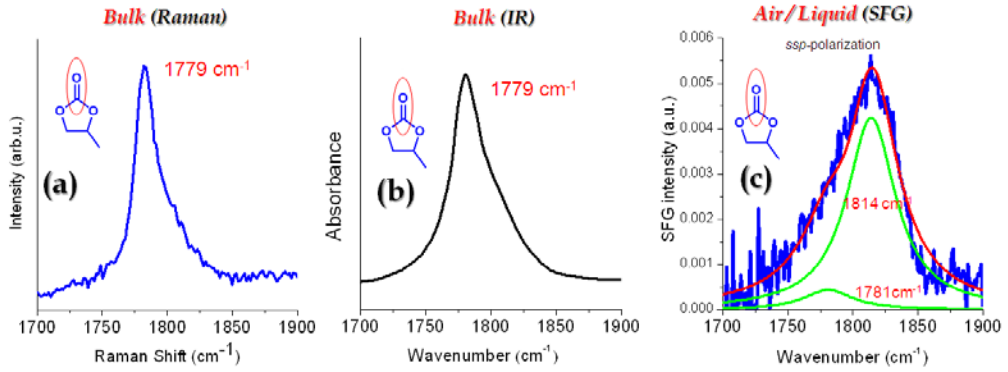

Fig.2 SFG Raman and IR spectrum of PC in Bulk and SFG Spectra of PC at Air/Liquid Interface.

Secondly, we evaluated structure at the carbon surface in air by SFG spectroscopy. Figure 3 shows SFG spectra at different IR central wavelength before normalization. As the central wavelength of IR excitation beam changes from 5450 nm (blue) to 5750 nm (pink), one is able to see an additional dip around 1718 cm^{-1} on the top of the nonresonant background otherwise an uniform and symmetric background peak should be observed. This novel signal is attributed to the carbonyl species on the carbon thin-film surface prepared by the thermal evaporation method. This indicates that the carbon film has already been partially oxidized. This feature has also been confirmed by *ex situ* XPS measurement.

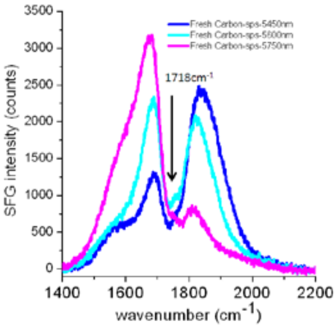

Fig.3 Original SFG Spectrum of Carbon Film with *sps*-polarization at different center wavelength of IR.

Furthermore, the carbon electrode / PC solvent interface was investigated by *in situ* SFG spectroscopy. The detailed results will be given in the presentation.

【Reference】

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