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学位論文内容の要旨

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学位論文題名

Study of molecular structure on carbon surface in nonaqueous electrolyte solution by sum frequency generation vibrational spectroscopy

(非水電解質溶液中におけるカーボン表面の分子構造に関する和周波発生振動分光研究)

Carbon is widely used as electrode materials in both industrial and fundamental applications due to their low cost, wide potential window, high electrocatalytic activity and stability in the electrolyte solutions. To learn about the interface between carbon and electrolyte solutions is of great significance to the developments of both the energy conversion technologies and the fundamental chemistry studies. The carbon/solution interfaces govern many fundamental processes such as adsorption/desorption equilibrium, deposit nucleation, Li-intercalation, solvent decomposition and reaction kinetics, which constitute kernel working mechanisms of the electrochemical devices and have been important research areas for many years. Although the structures and properties of the bulk carbon materials have been extensively investigated by many well commercialized techniques, such as Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and electrochemical quartz crystal microbalance, the knowledge about the molecular structure at the carbon/solution interface is still limited due to the low interfacial selectivity and sensitivity of these techniques to the molecular structures on the carbon surface .

As a second order nonlinear vibrational spectroscopy, sum frequency generation (SFG) vibrational spectroscopy has been proven as a powerful probe with extremely high sensitivity and selectivity to interfaces. By overlapping a tunable IR laser and a visible laser of a fixed frequency on the carbon/solution interface, one is able to determine a vibrational spectrum from the carbon surface. In the present studies, the SFG observation with internal reflection configuration was employed to investigate the molecular structure and behavior on the carbon/solution interfaces under *in situ* conditions for the first time.

In Chapter 1, the background of the carbon materials is briefly introduced. Then, the previous studies on the carbon/solution interfaces by different surface analysis techniques are reviewed, especially those related to Li-ion batteries. Finally, the objective and the outline of the present thesis are illuminated.

In Chapter 2, it gives a general theoretical background of SFG approach. The data analysis method and the optical setups of the SFG instruments are also demonstrated.

In Chapter 3, the preparation and characterization methods of the carbon materials including carbon thin-films and graphene monolayer are described. The carbon thin-film is deposited by thermal evaporation and then subjected to reductive treatment in hydrogen at elevated temperature to remove the surface-bounded oxygen species. The graphene monolayer was prepared by chemical vapor deposition on the copper surface and then transferred to the optical substrate surface for the subsequent experiments.

In Chapter 4, it describes *in situ*-SFG observations of the adsorption structures of the organic carbonate solvents which are widely used in Li-ion batteries, i.e., dimethyl carbonates (DMC) and propylene carbonate (PC), on the surface of a carbon thin-film under the internal reflection configuration. Both DMC and PC exhibit two different adsorption orientations on the carbon surface. One is pointing its C=O group towards the carbon surface and the other one is pointing away from the carbon surface. In a mixed solvent of PC and DMC, PC is preferentially adsorbed on the carbon surface in comparison to DMC. Furthermore, the adsorption of vinylene carbonates (VC) and fluoroethylene carbonates (FEC), which are commonly used as electrolyte additives in the Li-ion battery, was also evaluated by SFG vibrational spectroscopy. It is found that the additives show a higher propensity to align on the carbon surface with respect to DMC but is comparable to that of PC. The different roles of the organic carbonate solvents in the formation of the solid electrolyte interphase (SEI) are discussed, in comparison with those of electrolyte additives. The present study is considered to provide the fundamental understanding on the interfacial structure and the SEI formation on the carbon anode surface of Li-ion batteries.

In Chapter 5, it reports the *in situ* SFG observations of the adsorption structures of organic solvents, dimethyl sulfoxide (DMSO) and PC, on the graphene monolayer electrode surface during oxygen reduction and oxygen evolution reactions (ORR/OER) using the internal reflection configuration. The coverage of the DMSO adsorption on the graphene electrode surface reversibly changes during ORR/OER cycles in Li-free and Li-contained DMSO-based electrolyte solutions saturated by oxygen. These behaviors are attributed to the reversible adsorption/desorption of DMSO and the lithium superoxide/peroxide during the ORR/OER. By contrast, the PC solvents are found to be unstable and decomposed during the ORR process in the PC-based electrolyte solutions, which is assigned to the oxidative decomposition by the superoxide generated during the ORR. The present study provides important information of the behaviors of the solvent molecules on the carbon cathode surface during the ORR/OER, which promotes a better understanding on the reaction mechanism and will help to find more suitable solvents for the Li-O₂ secondary battery.

In Chapter 6, it summarizes the main results and the general conclusions of this thesis.