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

Peng Qiling

Summary

【Purpose】
Carbon materials are widely used as electrode due to their low cost, wide potential window, high electrocatalytic activity and stability in the electrolyte solutions. To understand 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 (FT-IR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrochemical quartz crystal microbalance (EQCM), the knowledge about the molecular structure at the carbon/solution interface is still limited due to the low interfacial selectivity and sensitivity.

But, deeper understanding for the molecular structure of the carbon/solution interface will be helpful for the fundamental development of energy storage techniques such as Li-ion secondary battery and Li-O\textsubscript{2} secondary battery. So far, there have been only limited previous researches on the carbon electrode/electrolyte interfaces by the surface-sensitive vibrational spectroscopy. This thesis will focus on investigating the molecular structures on the carbon surface in nonaqueous electrolyte solution with the SFG vibrational spectroscopy using the internal reflection geometry.

【Methods】
Sum Frequency Generation (SFG); Atomic Force Microscope (AFM); Raman Spectroscopy; X-ray Photoelectron Spectroscopy (XPS); Chemical Vapor Deposition (CVD);

【Experimental】
Figure below shows a schematic structure of a SFG cell we designed and was made of Kel-F for the in situ SFG observation on the carbon/solution interface. The visible and IR beams spatially and temporally overlapped on the interface between carbon (or graphene) and solution with incident angles of 70° and 50°, respectively, from the backside of the substrate. With such a configuration, no beam will pass through the bulk solution in comparison with the thin-layer cell. The energy of the IR beam was efficiently attenuated and the local electric fields on the carbon surface are significantly enhanced.
Two lithium wires were installed in the SFG cell as reference and counter electrodes in the nonaqueous electrolyte solutions. The carbon thin-film and single layer graphene supported on the CaF₂ prism surface was a working electrode, whose potential could be modulated for the electrochemical measurement coupled with SFG characterization.

【Conclusion】
In the thesis, the optical design for the in situ-SFG observation has been realized using an internal reflection configuration to avoid the problems in the thin-layer cell design used in the previous SFG measurements. With the new setup, the IR absorption by solvent is largely reduced while the local electric field intensity on the sample surface and mass diffusion conditions are significantly improved. The optimum optical design enables us to characterize the vibrational spectroscopy of organic solvents and additives on the surfaces of model carbon electrodes at a molecular level.

The interfacial structures of solvents and electrolyte additives used in Li-ion battery, such as propylene carbonate (PC), dimethyl carbonate (DMC), vinylene carbonates (VC) and fluoroethylene carbonates (FEC), on the carbon/solution interface have been investigated by in situ SFG at a molecular level. Two adsorption orientations were observed for both DMC and PC. In a mixed solution, PC is preferentially adsorbed on the carbon surface in comparison with DMC. Furthermore, the adsorption structures of VC and FEC, the common additives in the electrolyte solutions of the Li-ion battery, were also evaluated. It was found that these additives show a propensity to align on the carbon surface with respect to DMC, but comparable to PC. This information is extremely important to understand the formation mechanism of SEI on the carbon cathode surface for the Li-ion battery.

The adsorption structures of dimethyl sulfoxide (DMSO) and PC on a well-defined graphene monolayer electrode surface have been evaluated by the same method during the oxygen reduction and oxygen evolution reactions (ORR/OER) for Li-O₂ battery, which was conducted under electrochemical potential control for the first time. In the
O₂-saturated DMSO-based electrolyte solution, the coverage of DMSO adsorbed on the graphene surface reversibly changes during the ORR/OER due to the preferential adsorption of O₂⁻ and Li₂O₂. In the O₂-saturated PC-based electrolyte solution, the coverage of PC adsorbed on the graphene surface irreversibly changes during the ORR/OER. This is attributed to the instability of PC molecules in the presence of O₂⁻ species which oxidatively decompose the PC during the ORR. One is expecting to establish a general rule for selecting suitable solvents for Li-O₂ batteries in near future.

The knowledge about the behaviors of solvent molecules at the specific carbon/electrolytes in the electrochemical environments promotes further understanding on the roles of solvents during the charge/discharge cycles in the secondary batteries, which will contribute to the practical development of the energy storage technologies.