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論 文 要 旨
THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

Lithium-Intercalated Carbon Electrodes and Their Electrochemical Behaviors in Aqueous Solution（リチウムをインターカレートした炭素電極の水溶液での電気化学挙動）

Chapter 1 General introduction

Graphite intercalation compounds have received much attention because of their unique structures and promising applications for decades. They are formed by the insertion of atomic or molecular layers of a different chemical species called an intercalant accommodated between the graphene layers of graphite which is highly oriented in c-axis and random in a- and b-axes orientation. This structure is of great interest because intercalant species diffuse between graphene layers in the processes of intercalation and deintercalation.

Lithium intercalated graphite exhibits much negative potential close to lithium foil, less reactivity and good reversibility, which became the state-of-the-art anode material of lithium ion battery. And it plays an important role in realizing the lithium "rocking chair" battery because it solved the safety problem of lithium ion battery and commercialized the "rocking chair" system. Consequently, a great number of researches were conducted for this material.

Lithium intercalation into graphite is a staging process, which is characteristic of structure and potential profile. In other words, this staging process is a phase transition process. The kinetics of staging process is closely related to the energy required to overcome the force of Van der Waals between adjacent graphene layers and the repulsive interaction between guest species of lithium.

Lithium could be intercalated into graphene layers of graphite through edge plane and the defect "hole" of basal plane. When lithium is inserted into graphene layers of graphite, the process is called “intercalation”. When lithium is deinserted from graphene layers of carbon, the process is called “deintercalation”.

The main purpose of this thesis is to study the electrochemical behaviors of lithium-intercalated carbon electrodes in aqueous solution. Two typical kinds of carbon electrodes have been chosen: glassy carbon (GC) with a disordered structure and highly oriented pyrolytic graphite (HOPG) with perfect stacking graphen layers.

Chapter 2 Lithium intercalation into graphene ribbons of glassy carbon

Through XPS, XRD and cyclic voltammetry (CV), it was confirmed that the lithium intercalation into graphene ribbons of the GC electrode substrate during the lithium electrodeposition in PC solution containing 0.1 M $LiClO_4$ and the lithium deintercalation during the corresponding oxidation process take place. The shift of the (002) Bragg peak to a smaller value of 2θ was observed in the XRD pattern for the lithium – electrodeposited GC powder compared with that for the GC powder. This provided a direct evidence of the lithium intercalation into graphene ribbons of the GC which are stacked in parallel. The formation of Li graphite intercalation compounds, LiC_{6n}, was also confirmed by the XPS measurements. CV was used to characterize the lithium intercalation / deintercalation process. In addition, the results obtained suggested that the lithium insertion / deinsertion to / from the cavities such as microvoids of the GC electrode substrate may occur along with the lithium intercalation / deintercaltion.

Chapter 3 Electrochemical behavior of lithium intercalated glassy carbon electrode in aqueous solution

In Chapter 3, the electrochemical behavior of lithium-intercalated glassy carbon (GC-Li) electrode in aqueous solution was investigated. GC-Li electrode showed a potential-independent current in the potential range from -0.2 to 1 V (vs. Ag/AgCl (KCl sat.)). Both anodic and cathodic currents are positive resulting from the oxidation of lithium deintercalated from GC-Li electrode. The whole process would be mainly controlled by lithium diffusion (solid state) from GC-Li electrode substrate to the electrode surface (edge site), the step of lithium oxidation on the electrode surface and the leaving step of lithium ion from its original edge site to solution. The third step was considered to largely affect the whole oxidation process. Consequently, the step of lithium ion leaving from its original edge site is the rate-determining step.

Chapter 4 Lithium intercalated highly oriented pyrolytic graphite and its electrochemical behavior in aqueous solution

In Chapter 4, the lithium electrodeposition was performed at edge plane pyrolytic graphite (EPPG) and basal plane pyrolytic graphite (BPPG) electrodes. The electrochemical behaviors of the two resulting electrodes (EPPG-Li and BPPG-Li) suggested that lithium could be intercalated into graphite structure through edge plane but not basal plane. The perfect structure of EPPG electrode facilitates proposing the model for the electrochemical process of EPPG-Li electrode in aqueous solution. The potential-independent anodic and cathodic currents arise from the oxidation of lithium at the edge site of electrode surface to donate an electron to the external circuit to form lithium ion, and then the resulting lithium ion leaves its original site to aqueous solution to produce a vacant site. There is a chemical potential difference of lithium between the sites occupied with lithium and vacant sites. This chemical potential difference is a driving force for lithium diffusion from the substrate to the vacant site of the electrode surface, resulting in a phase transition in EPPG-Li electrode.

Chapter 5 General conclusions

(1) Lithium could be intercalated / deintercalated into/from GC and EPPG electrodes, but not BPPG electrode.

(2)Lithium-intercalated carbon electrodes (GC and EPPG) show potential-independent positive current in the forward and backward potential scan during the CV measurement for the oxidation. The positive currents result from the oxidation of lithium deintercalated (and deinserted) from lithium-intercalated (and -inserted) carbon electrode.

(3)The electrochemical oxidation is not a usual one-dimensional diffusion-controlled process expected for large planar electrode. The whole oxidation process is mainly controlled by the processes of dissolution of lithium ion and the diffusion of lithium atom in solid state. And the dissolution (solvation) is considered as a rate-determining step.