MLF Experimental Report	提出日 Date of Report 2015.1.9
課題番号 Project No. 2014A0294 実験課題名 Title of experiment Effect of Additives on Carbon-Electrolyte Interfaces in Li-ion Secondary Batteries 実験責任者名 Name of principal investigator Masashi Harada 所属 Affiliation Toyota Central R&D Labs., Inc.	装置責任者 Name of responsible person Norifumi Yamada 装置名 Name of Instrument/(BL No.) SOFIA/BL16 実施日 Date of Experiment 2014.6.25 ~ 2014.6.26, 2014.11.7 ~ 2014.11.9

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

A model anode of carbon thin films was deposited on a titanium buffer layer formed on a silicon substrate by sputtering technique. [see Fig. 1]. The electrolyte was 1M $LiPF_6$ which was dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). To analyze the effect of an additive in the electrolyte solution, vinylene carbonate was added to the EC/DEC mixture with $LiPF_6$.

The structural change of the interface between the anode and the electrolyte by electrochemical potential was examined by using novel electrochemical apparatus designed for the NR measurements [see Fig. 2] The working electrode (WE) was a thin film of carbon and the counter electrode (CE) was a lithium foil.

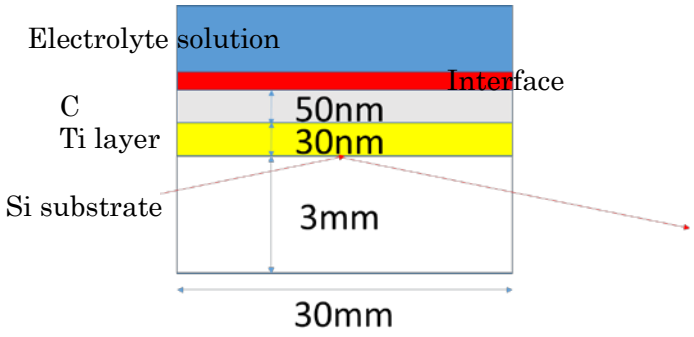

Figure 1 Multilayer structure of a model carbon anode in contact with an electrolyte solution.

Figure 2 Electrochemical cell for neutron reflectometry.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The incident angles of the neutrons were 0.3 °, 0.6 °, 1.2 °. The potential of the carbon anode against redox reaction of Li/Li^+ was controlled at 1.5 V, 1.0 V, 0.5 V, 0.05 V. The results of the neutron reflectivity measurements for the electrolyte solution without and with additives are shown in Figures 3(a) and 4(a), respectively. The spectra with a resolution $\Delta q/q$ = 2 % was obtained in about 1 hour at 300 kW. Critical angle and clear fringes were observed in the spectra of the model anodes. Moreover, we could find the change of the spectra by the potential, which should reflect the evolution of the interfacial structure between the electrode and the electrolyte.

The cross-section profiles of the scattering length density (SLD) were obtained by model fitting of the spectra, as shown in Figures 3(b) and 4(b). One extra layer at the interface of the electrode and the electrolyte was required for the fitting. Since the thickness and the SLD of the buffer and the anode layers should be unchanged by the potential, the fitting parameters of the buffer and the anode were globally fixed for the four spectra with different potential values. Therefore, the fitting parameters were the thickness and the SLD of the interfacial layer. It is evidenced that there is an interfacial layer with around 20 nm thickness and that the structure of the layer changes in a slightly different way for the two series of samples without and with additives.

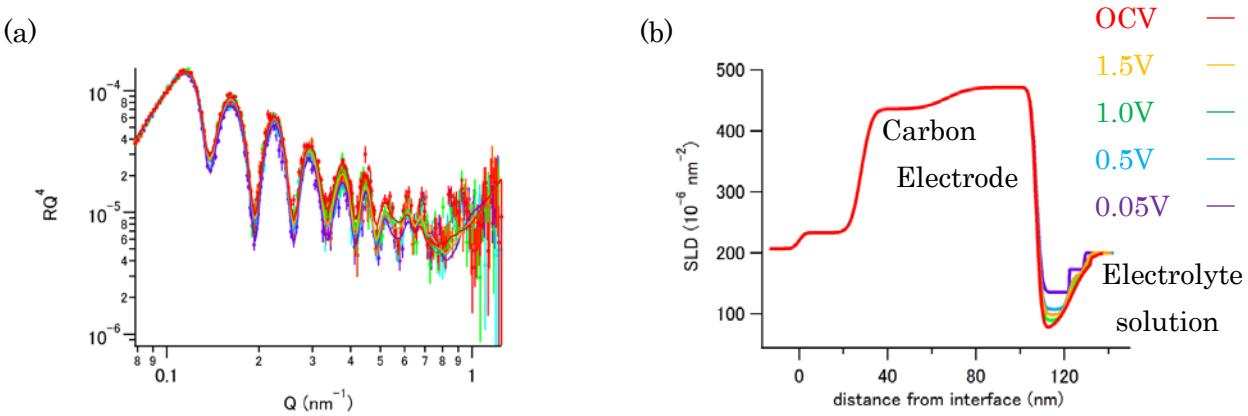

Figure 3 Neutron reflectivity spectra (a) and scattering length density profiles (b) for the model anode without additive in the electrolyte solution.

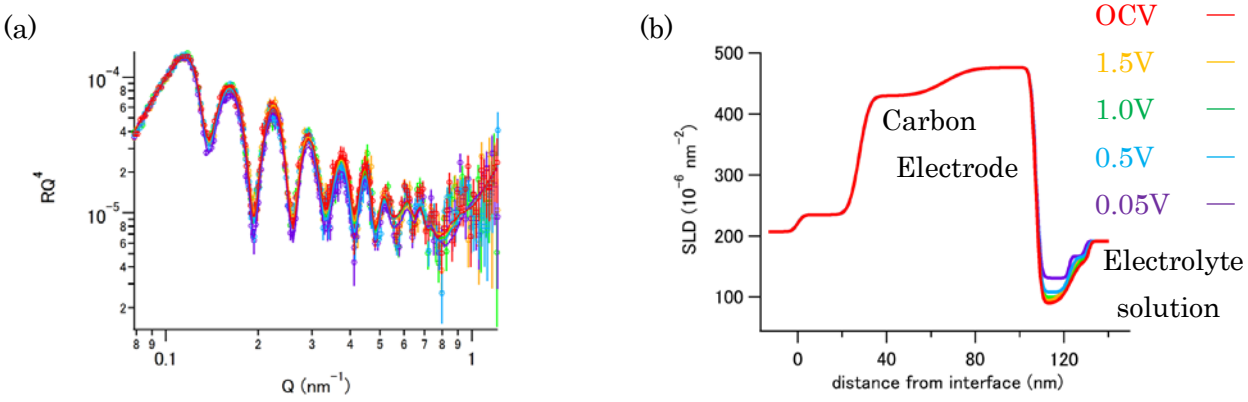

Figure 4 Neutron reflectivity spectra (a) and scattering length density profiles (b) for the model anode with additive in the electrolyte solution.