Operando XAFS Measurement for Electrochromic Ru-based Metallo-Supramolecular Polymer Devise

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Electrochromic (EC) materials have been studied in the fields of organic molecules, inorganic materials, organic polymers, and metallo-supramolecular polymers (MSPs),[1] where the redox reaction of the metal ion (or organic molecule) induces color change. In addition, EC materials such as WO_3 or NiO have been used for smart windows, EC display, and electronic paper. To understand the mechanism of electrochromism, it is important to track the oxidation state of the material.

The MSPs, prepared by a 1 : 1 complexation of metal ions with ditopic organic ligands, are a new type of coordination polymers and have been investigated for EC properties, ion conductivity, and luminescence.[1] Group 8 metal ions (M = Fe, Ru, Os ions) based MSPs (**polyM**) show clear EC, whereas **polyM(ii)** show a deep color and **polyM(iii)** show a transparent color, and in addition, they have been studied for use in EC displays with high durability.[1] Cyclic voltammetry (CV), electron spin resonance (ESR), and X-ray absorption fine structure (XAFS) analysis are representative methods used to observe the electronic state of materials. However, these methods either give averages or are challenging to measure operands. In this study, we performed operando time-resolved XAFS mapping measurements of electrochromic Ru-based MSPs devices.

Herein, we selected **polyRu** among the reported MSPs and tracked their electronic states of EC devices during electrochromism by operando time-resolved XAFS spectroscopies with a single photon counting X-ray detector. XAFS spectroscopy at the Ru K-edge was carried out at the BL36XU beamline of the SPring-8.

XANES spectra of the oxidized state (Ru^{3+}) and reduction state (Ru^{2+}) were observed, where the second peak intensity at 22140 eV is lower in the oxidized state than in the reduced state. This tendency is similar to reported Ru complexes.[2] The details of time-resolved XAFS measurements will be shown in the presentation.

In conclusion, we established the method for time-resolved XAFS mapping of Ru-based electrochromic devise. This result offers a new avenue for developing the strategy of design for metallo-supramolecular polymer.

1) M. Higuchi*, J. Mater. Chem. C,* **2014***, 2,* 9331–9341, 2) de Aguirre *et al. Nat. Chem.* **2020***, 12*, 1060–1066.