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X-ray Absorption Spectra of Lipid Bilayer Membranes in Electrolyte Solutions and Its Dependence on Cation Species

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The lipid bilayer is a self-assembled structure of amphiphilic lipid molecules. It is the fundamental structure of biomembranes such as cell membranes, which are the fields for the transportation of materials, information, and energy into and out of cells. All these physiological reactions proceed in the presence of electrolytes. Ions in the aqueous solution significantly influence physical properties and structures of lipid bilayers. Phosphatidylcholine (PC) is the most abundant lipid of eukaryotic cell membranes. Cations bind to the phosphate and carbonyl groups of PC. However, the affinity of cations to PC and effects of cations to molecular orientation are still controversy especially in the fields of theoretical simulations. We aim to determine the binding affinity of cations to lipids in aqueous solutions experimentally, by means of X-ray absorption spectroscopy (XAS) [1]. Recently, we measured the dependence of O-K edge XAS spectra of DOPC bilayer on Na^+ concentration in the aqueous solution [2, 3].

Supported lipid bilayers (SLBs) of dioleoyl-PC (DOPC) were formed on the Si_3N_4 membranes of the XAS flow cell [1] by the vesicle fusion method in a buffer solution (KCl 100 mM, HEPES 25 mM/ pH 7.4 KOH). The K^+ concentration ($[K^+]$) was varied by exchanging the buffer solution in the flow cell in in the range of $[K^+]$ = 2.1 – 510.4 mM. The O-K edge XAS spectra of SLB were obtained at the energy range of 527 – 535 eV. The X-ray incident angle of 35º. The XAS spectrum of the Si_3N_4 membrane without SLB was subtracted from that with SLB.

The O-K-edge spectrum of DOPC appeared at 531 - 533 eV [2, 3]. It consists of 1s→π* transitions of double-bond oxygens in the phosphate and carbonyl groups on the PC headgroup: two components attributed to the P=O in the former, and one component attributed to the latter. We measured XAS spectra at the X-ray incident angle (T) of 35º. We obtained a specific dependence of the P=O peak at the lower energy on $[K^+]$: its position was little affected by $[Na^+]$ in the range of 2.1 – 10.4 mM and shifted to higher energy by ~0.4 eV at $[K^+]$ = 20.4 mM, while the position showed slight change at $[K^+] \geq 50.4$ mM. The former tendency at was similar to that of Na^+ at $[Na^+] \leq 20.4$ mM, but latter was different from the peak shift and broadening observed at $[Na^+] \geq 50.4$ mM [2, 3].

The inner-shell quantum chemical calculation [4] of O K-edge spectrum of P=O indicated that coordination of K^+ to the phosphate group causes higher-energy shift of P=O peaks. The XAS spectra shows the difference in the coordination affinity between K^+ and Na^+. The effects of the cation species on the XAS components will be evaluated by the theoretical calculations.

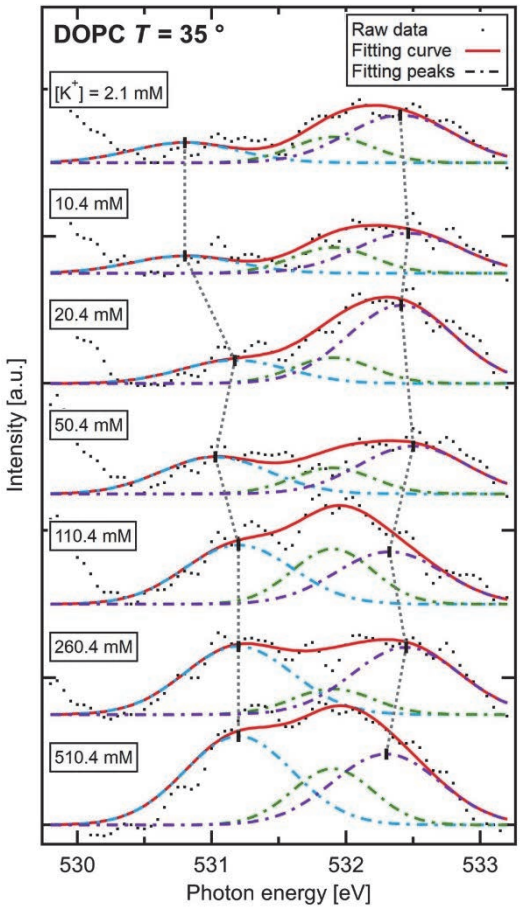

Fig. 1. O K-edge XAS spectra of DOPC-SLB at $[K^+]$ = 2.1 – 510.4 mM obtained at the X-ray incident angle of 35°. Black dotted curves represent raw data. Dashed curves and red solid curves show deconvoluted components and their summation, respectively.

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Surface Effect on the Layer Structure in the Chiral SmC Variant Phase Delicate Balance of Ferroelectricity and Antiferroelectricity by Resonant Soft X-ray Scattering (RSoXS) at UVSOR

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The ferroelectricity and antiferroelectricity have been found in the tilted chiral smectic phases, called SmC* and SmC_A*, respectively. By competition of SmC* and SmC_A*, several phases with narrow temperature range were often found, called subphases. Subphases have are defined as the relative ratio of anticlinic and synclinic ordering, q_T. The structures of subphases becomes decisive using resonant X-ray scattering (RXS), and one of authors (YT) discovered new subphases with 6-, 7-, 8- and 10-layer periodicities[1,2].

In a certain chiral binary system, it was found that clear phase transition between subphases seems not to be seen[2]. The composed compounds do not have a specific atom, so that resonant soft x-ray scattering (RSoXS) has been applied to this study, and we directly observed the structure of continuous change between SmC* and SmC_A* using wide angle RSoXS.

The experiment was performed at BL3U of UVSOR. Used sample is a mixture of MC881 and MC452, as shown in Fig. 1. Figure 1(c) shows the phase diagram around the critical mixing ratios. In this study, two types of sample cells were prepared; a planar sub-micron thick sandwich cell whose substrates are 100 nm-thick Si_3N_4 membranes, and the liquid-crystal-filled grid mesh for electron transmission microscopy. The scattering was detected by CCD (ANDOR DO940P-BN). Incident X-ray beam was tuned between 270~300 eV, and carbon K-edge energy was 284.5 eV in the mixture.

RSoXS intensity profiles of the mixture of 55.7wt% MC452 at 24°C in the sandwich cell and the mesh are shown in Figs. 2(a) and (b), respectively. In Fig.2(a), a strong sharp peak was observed at Q ~ 1.1 nm^{-1} suggesting to the bilayer structure, while a splitted strong peak at Q ~ 0.55 nm^{-1} corresponding to the 4-layer periodicity was observed in Fig. 2 (b). (Peak splitting is caused by the helical structure.) This difference is considered to be caused by the surface effect. The gap of membrane sandwich cell was verry thin. Hence the strong surface effect appears and molecular orientation is limited to the substrate surface plane. On the other hand, in the mesh cell, the surface effect is weak. As a result, the molecular orientation has the degree of freedom in the azimuthal angle as a bulk state. The difference in structure between these two cells is believed to be due to the surface effects mentioned above, and the small energy difference between the ferroelectric and antiferroelectric orders.

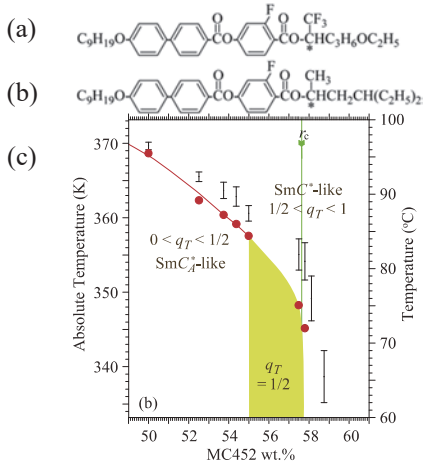

Fig. 1. Chemical structures of (a)MC452 and (b) MC881, and (c)the phase diagram referred from [3].

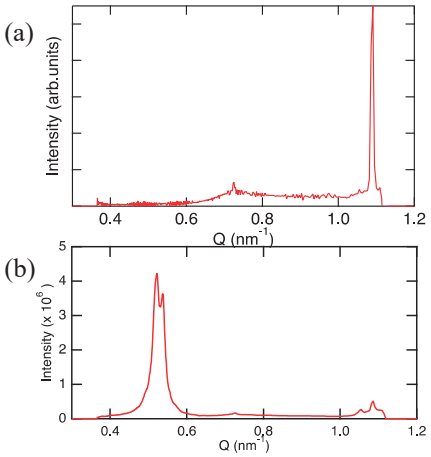

Fig. 2. RSoXS intensity profiles of the sandwich cell (a) and the grid mesh (b) of the mixture of 55.7wt% MC452 at 24°C.

[1] Y. Takanishi *et al*., Phys. Rev. E **87** (2013) 050503 (R).
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Oxygen K-Edge Soft X-Ray Absorption Spectroscopy of Pd/CeO_2 Catalyst for DC-Assisted Dry Reforming of Methane

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Chemical utilization of methane (CH_4) and carbon dioxide (CO_2) is of great importance because both are greenhouse gases. Catalytic dry reforming of methane (DRM; $CH_4+CO_2 \rightarrow 2CO+2H_2$) is therefore much attractive reaction in which CH_4 and CO_2 are converted syngas, i.e., the mixture of carbon monoxide (CO) and hydrogen (H_2). In particular, DRM can be a powerful solution of biogas (the mixture of CH_4 and CO_2) utilization [1].

In the conventional DRM induced by thermal catalysis, high reaction temperatures above 973 K are required for activation of CH_4 and CO_2 because both molecules are highly stable. From the thermodynamic point of view, high reaction temperatures are also profitable for achieving high equilibrium conversion. However, under the harsh reaction conditions, catalysts are rapidly deactivated by carbon deposition through CH_4 decomposition ($CH_4 \rightarrow C+2H_2$) and CO disproportionation ($2CO \rightarrow C+CO_2$). Therefore, non-thermal catalytic DRM processes at low temperatures are desirable for suppression of the coke formation and efficient energy utilization.

To promote DRM at low temperatures, we have developed DC-assisted catalysis in which constant DC of the order of a few mA is applied to the catalyst [2]. In this catalytic system, ceria (CeO_2)-supported metal catalysts exhibit high catalytic performance [2]. However, it remains a challenge to elucidate why DRM can be driven at low temperatures, although we reported the key role of surface lattice oxygen species [3]. In this study, to obtain microscopic insight into the reaction mechanism, we performed oxygen *K*-edge soft X-ray absorption spectroscopy (SXAS) of the CeO_2-supoorted palladium (Pd) catalyst.

Pd/CeO_2 was prepared by an impregnation method; firstly, CeO_2 (JRC-CEO-1; Catalysis Society of Japan) and distilled water were added to a flask and were stirred for 2 h, then palladium acetate (Kanto Chemical Co. Inc.) solved in acetone was added into the flask and was further stirred for 2 h. After the suspension was evaporated, the obtained powder was dried at 393 K and calcined at 773 K. For the SXAS measurement, the calcined powder was formed into a pellet.

The SXAS measurement was performed at the BL3U beamline of UVSOR-III synchrotron. After the sample was put on the cell, the chamber was evacuated by a turbomolecular pump. Then, the mixture of CH_4, CO_2 and He, was introduced in the chamber and DRM was induced by applying DC to the sample. SXAS spectra were measured in fluorescence yield mode with a silicon drift detector.

Figure 1 shows the O *K*-edge SXA spectra of the Pd/CeO_2 before and after the reaction. In the spectra before the reaction, two peaks at 529.8 and 532.9 eV were observed. These peaks are attributed to the hybridized O2p-Ce4f state at 529.8 eV and the hybridized O2p-Ce5d(e_g) state at 532.9 eV [4].

Compared with the spectra before the reaction, the two peaks derived from CeO_2 were shifted to the lower energy after the DRM reaction. The shift of the hybridized O2p-Ce5d(e_g) state indicates that a part of Ce^{4+} was reduced to Ce^{3+} during the reaction [5] whereas the shift in the hybridized O2p-Ce4f state suggest the change in the local environment of Ce^{4+}. These results suggest that the redox properties of Ce play a crucial role in the DC-assisted DRM reaction.

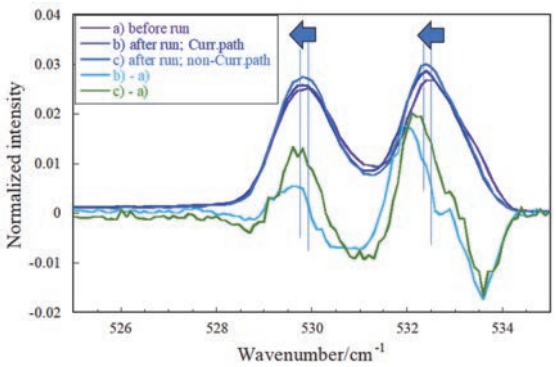

Fig. 1. Oxygen *K*-edge spectra of 1wt%Pd/CeO_2 before and after the DRM reaction. The spectra were measured in fluorescence mode using a silicon drift detector. The DRM reaction was performed by applying DC to the catalyst at $P_{CO2}=P_{CH4}=P_{He}=5$ kPa.

[1] M. Usman *et al.*, Renew. Sustain. Energy Rev. **45** (2015) 710.
[2] A. Motomura *et al.*, RSC Adv. **12** (2022) 28359; A Motomura *et al.*, Chem. Lett. **52** (2023) 259.
[3] N. Nakano *et al.*, RSC Adv. **12** (2022) 9036.
[4] L. Amidani *et al.*, J. Phys. Chem. *C* **127** (2023) 3077.
[5] A.B. Altman *et al.*, Dalton Trans. **45** (2016) 9948.

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XAS Measurements for Grahpene Oxide Aqueous Solutions

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XAS measurements for liquid samples have been enabled at UVSOR BL3U, giving new insights for physicochemical properties of materials [1]. We have achieved O-K edge XAS measurements for cellobiose aqueous solutions and found that XAS signals can be simulated with CP2K and hydrogen bonding with water molecules affect the relative intensity of XAS peaks [2]. In this study Graphene oxide (GO) was chosen as a target molecule. GO is widely used as a catalyst support due to its hydrophilic, acidic, large surface area, and easy modification properties. However, although several structural models have been proposed, none have been conclusively established. We are searching for a suitable structural model for graphene oxide based on quantum chemical calculations, clarifying the dependence of the model on the carbon number, oxygen content, and degree of unsaturation. In particular, we will clarify the functional group structure and carbon defects contained therein and the associated structural features. To verify this, we will perform measurements using soft X-ray absorption spectroscopy and perform simulation calculations of the spectra to experimentally verify the structural model.

XAS measurements for liquid samples were conducted at UVSOR BL3U using facilities developed by Nagasaka et al. [1]. The liquid sample cell with Si3N4 membranes was adopted, where the thickness of the liquid layer was controlled by the He gas pressure around the cell. GO was prepared by the modified Hummers method [3] and aqueous solution was prepared by sonication of 2 hours.

Figure 1 shows C-K XAS spectrum for GO (14 mg) in 10 ml water at room temperature. Three peaks at 285, 287 and 291 eV were observed. O-K XAS measurement was also achieved but due to the dominant contribution by water molecules it was difficult to assign peaks originated from GO (not shown).

We are also conducting computational study for obtaining typical structural formula of GO. In order to clarify the structure of graphene oxide, we performed a structure search using l-ADDF calculations using GRRM, sorted the resulting equilibrium structures (EQs) in order of energy, and enumerated the partial features within the structure for each EQ as structural features, thereby summarizing the energetically stable EQs and their structural features. Multiple l-ADDF calculations with different calculation conditions were conducted, and the trends was clarified as to the results of the structure search (calculation time, number of EQs obtained, number of structural features obtained, and energy width of the EQs obtained) when changing LADD, Nlowest, and calculation level. We also compared previously proposed structures and found the modified structure which exhibits the stabilized total energy with a modified partial structure as shown in Fig. 2. XAS simulation calculation using the obtained GO formula is undertaken to assign the peaks in the experimental result.

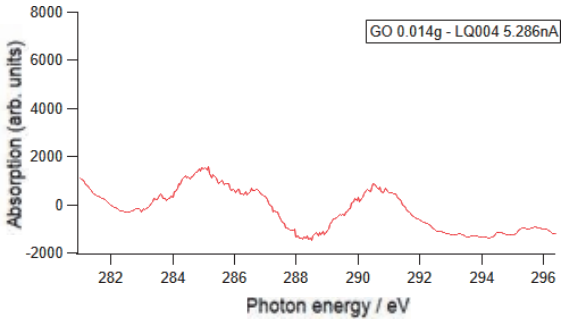

Fig. 1. C-K XAS spectrum for GO (14 mg) in 10 ml water at room temperature.

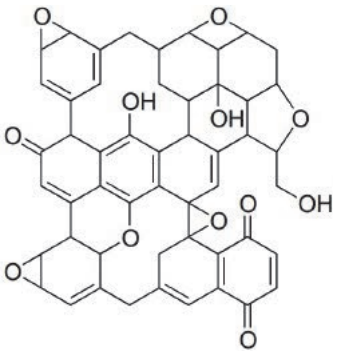

Fig. 2. One of the GO models obtained by GRRM calculation.

[1] M. Nagasaka *et al.*, J. Electrosc. Relat. Phenom. **200** (2015) 293.
[2] D. Akazawa *et al.*, J. Chem. Phys. **156** (2022) 044202.
[3] V.B. Saptal *et al.*, Chem. Sus. Chem. **9** (2016) 644.

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Salt-Specific Effect on the Solubility and Aggregation of 1-butanol in Water

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The Hofmeister series has continued to a topic of interest across a variety of fields [1], and the Hofmeister anion series is typically represented by $CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$. The solubility and aggregation of solute molecules in water has been influenced with the addition of these Hofmeister anions. In this study, the salt-specific effect on the degree of aggregation of 1-butanol molecules in aqueous solutions were studied using C K-edge X-ray absorption spectroscopy (XAS) [2].

The C K-edge XAS experiments were performed at BL3U using the transmitted-type liquid cell, whose details were described previously [3, 4]. The liquid cell was at an ambient pressure in helium gas, where a liquid layer was sandwiched between two Si_3N_4 membranes with a thickness of 100 nm. The thickness of the liquid layer was precisely controlled by adjusting the helium pressure for obtaining appropriate absorbance of soft X-rays. XAS spectra were obtained using the Lambert-Beer law, $\ln(I_0/I)$, where I and I_0 are the transmission signals of aqueous butanol solutions including salts and the solutions without 1-butanol, respectively.

Figure 1 shows C K-edge XAS spectra of 0.2 M aqueous 1-butanol solutions including different salts, where 1 M $NaClO_4$, 1 M NaCl, and 1 M Na_2SO_4 are dissolved. The temperatures of aqueous solutions were kept at 25 °C. The XAS spectra consists of five broad peaks, which were assigned using the inner-shell calculations: The lowest peak is assigned to the transition of the CH_3 C1s electrons to the 3s-type Rydberg orbitals. The second peak is assigned to the transitions of the CH_2 C1s electrons in the center part of the butyl group to the 3s-type Rydberg orbitals. The third peak is assigned to the transitions of the CH_3 C1s electrons to the 3p-type Rydberg orbitals. The fourth peak is assigned to the transitions of the CH_2 C 1s electrons in the center part of the butyl group to the 3p-type Rydberg orbitals. The fifth peak is assigned to the transitions of the CH_2 C1s electrons connected to the hydroxyl groups to the 3s-type Rydberg orbitals.

The peak intensity at 288.5 eV in the XAS spectrum of 0.2 M aqueous 1-butanol solution is higher than that in the spectrum of neat 1-butanol liquid. It is because 1-butanol molecules are remarkably isolated in the dilute aqueous solution. This tendency is same as the C K-edge XAS spectra of aqueous methanol and ethanol solutions [5, 6]. It means that the aggregations of 1-butanol molecules in aqueous solutions would be evaluated from the peak intensities at 288.5 eV.

In the C K-edge XAS spectra of 0.2 M aqueous 1-butanol solutions shown in Fig. 1, the peak intensities at 288.5 eV are decreased with the order of $NaClO_4$, NaCl, and Na_2SO_4 from those with no salt condition. It means that the aggregations of 1-butanol molecules by adding salts are increased with the order of $NaClO_4$, NaCl, and Na_2SO_4. It means that the aggregations of 1-butanol molecules follow the Hofmeister anion series. These results provide molecular insights into how ions affect solute solubility and solute-solute aggregations for other hydrophobic molecules. The C K-edge XAS measurements are useful for evaluating the aggregations of hydrophobic molecules in aqueous solutions.

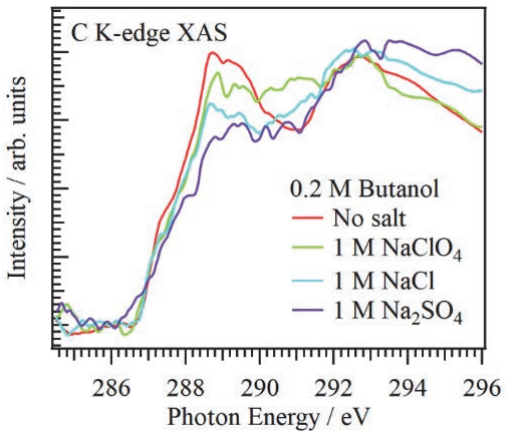

Fig. 1. C K-edge XAS spectra of 0.2 M aqueous 1-butanol solutions including different salts (1 M $NaClO_4$, 1 M NaCl, and 1 M Na_2SO_4).

[1] F. Hofmeister, Arch. Exp. Pathol. Pharmakologie **24** (1888) 247.
[2] Y. Yao *et al*., Physica A **647** (2024) 129917.
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[5] M. Nagasaka *et al*., J. Phys. Chem. B **118** (2014) 4388.
[6] M. Nagasaka *et al*., J. Phys. Chem. B **126** (2022) 4948.

BL3U

Structure Analysis of Organic Thin-Film Solar Cells Using Resonant Soft X-ray Scattering Technique

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Resonant soft X-ray scattering is an innovative technique for analyzing chemical-specific structures in material science. Conventional small-angle X-ray scattering (SAXS) has been widely used to analyze nanostructures within materials. However, when analyzing polymer composites, SAXS faces significant challenges due to the lack of contrast between polymers composed mainly of light elements. This makes it difficult to determine how these polymers mix and interact. For instance, in organic thin-film solar cells, efficient charge transfer is achieved when two molecules form a bulk heterojunction structure. However, this structure is challenging to measure using conventional SAXS.

Resonant soft X-ray scattering (RSoXS) enhances scattering from specific molecules by utilizing their resonant energy differences. This technique takes advantage of the slight differences in resonant X-ray energies between two molecules to clarify their structures and arrangements. This allows for detailed analysis of the internal structures of polymer composites. In this work, we show an example application of RSoXS in the analysis of organic thin-film solar cells.

Our sample is an organic thin film composed of [6,6]-Phenyl-C61-butyric Acid Methyl Ester (PCBM) and Poly(3-hexylthiophene-2,5-diyl) (P3HT) spin-coated on a 100 nm thick Si3N4 membrane, and has a bulk heterojunction structure separated at the nanoscale as shown in Fig. 1. The thickness of this film is about 200 nm.

The experiment was performed at UVSOR BL3U. The soft X-ray energy was 260 eV for non-resonance and 284 eV and 286 eV for resonance, respectively. The camera length was 100 mm, and the scattered light was observed with a soft X-ray camera (Andor BN940P).

Figure 2 shows the scattering profile at the photon energy of 260, 284, and 298 eV. The horizontal axis is the scattering vector q [nm^{-1}], and the vertical axis is the scattering intensity. No strong scattering peak was observed in the non-resonance case of 260 eV. This means that there is no difference in the complex dielectric constant of the two molecules, so there is no contrast in the scattering process. On the other hand, at 284 eV, close to the resonance energy of PCBM, a strong peak was observed at q=0.2 nm^{-1}. This indicates that PCBM has a spatial scale of about 30 nm. On the other hand, at 298 eV, where scatterings from P3HT are enhanced, a peak was also observed at q=0.1 nm^{-1}. This means that P3HT has a spatial scale of about 60 nm.

In our work, it has been shown that the structure of each polymer can be analyzed by using resonant soft X-ray scattering. We will continue to conduct detailed analysis.

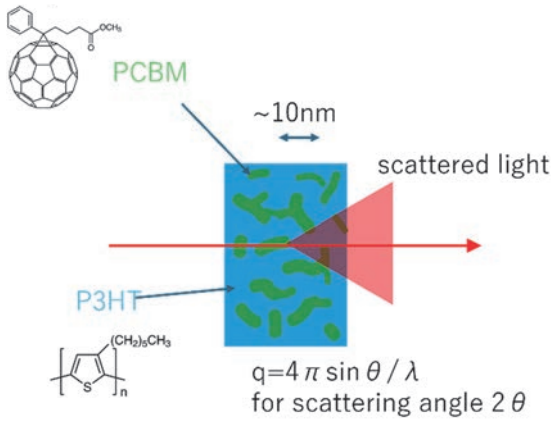

Fig. 1. Schematic view of the organic thin film, where bulk heterojunction of PCBM and P3HT is formed.

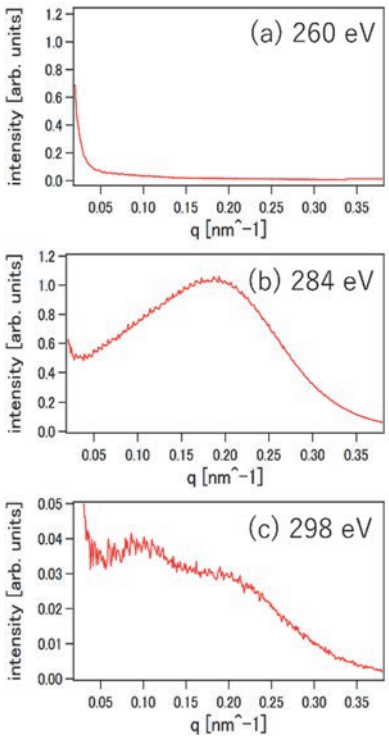

Fig. 2. Scattering profiles for the organic thin film at the photon energies of (a) 260 eV, (b) 284 eV and (c) 298 eV.

BL3U

Observation of O K-Edge X-Ray Absorption Spectrum of μ-Oxo-Bridged Iron Phthalocyanine Dimer

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Coordination of oxygen atoms to the iron porphyrinoids has long been attracted interests of chemists since interactions of oxygen atoms with iron center of iron porphyrin are quite important in various biological processes such as oxygenation, oxygen carrying, and so on. It is well-known that iron(II) porphyrinoids including iron porphyrin and iron phthalocyanine tend to form μ-oxo-bridged dimers as described in Fig. 1 under air [1]. These μ-oxo-bridged dimers of iron porphyrinoids can act as an oxygenation catalyst for various organic chemicals under photoirradiation in the presence of O_2.

To the best of our knowledge, soft X-ray XAS studies of μ-oxo-bridged iron porphyrinoid dimers have not been reported yet, although there are some reports on hard X-ray XAS studies. Therefore, the purpose of this work is to investigate μ-oxo-bridged iron phthalocyanine dimer by soft X-ray XAS. We prepared a μ-oxo-bridged iron phthaloycyanine dimer having 8 peripheral *tert*-butyl units **1** and a monomeric iron(III) phthalocyanine chloride having 4 peripheral *tert*-butyl units **2**. The use of soft X-ray XAS is advantageous because direct and selective observation of both oxygen and iron atoms in an μ-oxo-bridged dimer become possible since the soft-X-ray region include both of the K-edge of oxygen and L-edge of iron.

O K-edge XAS measurements of **1** and **2** in solution were performed by using a beamline equipped with a transmission-type liquid flow cell in BL3U of UVSOR [2]. The spectra were obtained based on the Lambert-Beer law, $\ln(I_0/I)$, where I_0 is the transmission signals of benzonitrile and I is those of **1** or **2**.

Fig. 2 shows a comparison of the O K-edge XAS spectra obtained for **1** and **2** in benzonitrile (30 mM). The blue spectrum represents that of **2** having no oxygen-containing moieties, where small amount of silicon oxide on Si_3N_4 membrane and H_2O in benzonitrile were observed. It is considered that the μ-oxygen of **1** should show double bond character due to the interaction of p-orbitals of the μ-oxygen atom with the d-orbitals of the iron atom of two iron porphyrins. It is known that, generally in the O K-edge XAS spectra, the peaks of oxygen having double bond character tend to appear at lower energy than 534 eV, whereas the peaks of oxygen having single bond character appears at higher energy than 535 eV [3]. By comparing the spectra of **1** and **2**, we considered that the peak at 527 eV and/or 532–534 eV could be assigned to those of μ-oxygen of **1**. In order to identify the peaks of μ-oxygen of **1**, we are going to measure the soft X-ray XAS of the solids of **1** and **2**. In addition, DFT calculations of XAS of **1** and **2** are also underway.

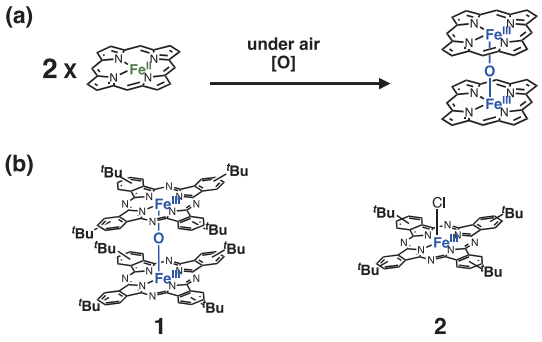

Fig. 1. Generation of μ-oxo-bridged iron porphyrin dimer from iron porphyrin.

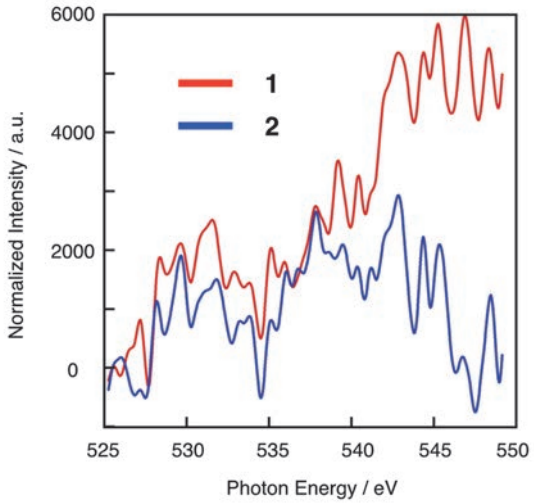

Fig. 2. Comparison of O K-edge XAS spectra of **1** and **2** in benzonitrile (30 mM) at 25 °C.

[1] S. P. Rath *et al.*, Coord. Chem. Rev. **337** (2017) 112.
[2] M. Nagasaka and N, Kosugi, Chem. Lett. **50** (2021) 956.
[3] M. Nagasaka *et al.*, Phys. Chem. Chem. Phys. **26** (2024) 13634.

BL3U

Soft X-ray Absorption Study of a Titanium-Oxide Photocatalyst Suspended in Water

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Material conversion on semiconductor photocatalysts is intensively studied worldwide. Downhill reactions, in which the Gibbs free energy decreases during the conversion of reactants to products, have been successfully integrated into our society [1]. Artificial photosynthesis, a category of uphill reactions involving the oxidation of water, is being developed for societal implementation in the near future [2]. In addition, fundamental studies are being conducted to uncover new scientific discoveries related to light-driven, efficient materials conversion.

In collaboration with Prof. Masanari Nagasaka of UVSOR, we apply soft X-ray absorption to the *in-situ* characterization of semiconductor photocatalysts suspended in water. An anatase TiO_2 photocatalyst (JRC-TIO-19 provided by Catalysis Society of Japan), was suspended in water. The suspended solution was adjusted with NaOH to pH 13. The pH adjustment was critical to suspend 100 nm TiO_2 particles long enough to pass through a liquid cell.

The liquid cell was mounted in BL3U. Oxygen K-edge and titanium L-edge absorption spectra were observed with a transmission setup [3] in the presence and absence of ultraviolet (UV) light for band-gap excitation. Soft X-rays transmitted through the suspended solution were detected with a silicon photodiode. The photodiode was capped with a 150 nm thick aluminum film (LUXEL, TF110) to minimize the contribution of stray UV light to the detector response (Fig. 1). The capping device is deposited at UVSOR. Users are encouraged to use the device when operating the photodiode under UV or visible light irradiation.

Figure 2 shows a Ti L-edge spectrum observed in the presence of UV light provided by a Hg–Xe lamp (200 W). In the Ti L-edge, electron transition from Ti2s and 2p to 3d orbitals of TiO_2 particles appears at 455–470 eV [4]. The Ti3p orbitals are hybridized with O2s and 2p orbitals to form the conduction band in TiO_2. The hybridized orbitals are split into t_{2g} and e_g levels according to the ligand field in TiO_6 octahedra.

The soft X-ray absorption of solutions has been successfully studied. Here, transmission measurement was achieved with a suspension. The extension to an *operando* study of the suspension under UV irradiation is possible.

This study was supported by JSPS KAKENHI (grant number 22H00344).

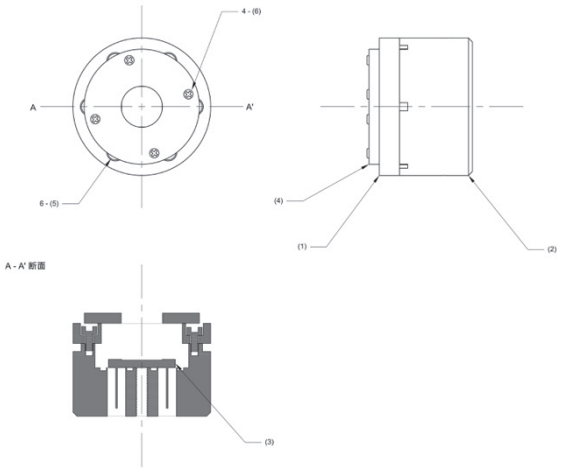

Fig. 1. A devise capping the photodiode with the aluminum filter for transmission detection of soft X-ray absorption spectrum under UV-light irradiation.

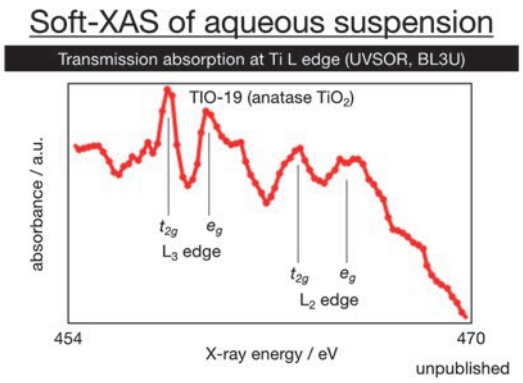

Fig. 2. Soft X-ray absorption of anatase TiO_2 photocatalyst particles (JRC-TIO-19) suspended in water at pH 13. Titanium L-edge spectrum was observed under UV light irradiation.

[1] A. Fujishima *et al.*, J. Photochem. Photobio. C **1** (2000) 1.
[2] H. Onishi, ChemSusChem **12** (2019) 1825.
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BL3U

Direct Observation of Solvation of Redox Species by Soft X-ray Spectroscopy toward Development of High Performance Thermo-Electrochemical Cells

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In the utilization of primary energy, approximately 50–60 % is discarded as unused waste, with around 70 % of this being low-grade waste heat. The recovery and reuse of low-grade waste heat using thermoelectric devices, which convert thermal energy into electrical energy, present an effective solution to the energy problem. Among various thermoelectric devices, thermochemical cells (TECs) utilizing liquid electrolytes have recently gained attention due to their high thermoelectric conversion efficiency [1]. The efficiency of thermoelectric conversion is evaluated by the dimensionless figure of merit as following:

$$ZT = \frac{S_e^2 \sigma T}{\kappa} \quad (1)$$

where S_e is Seebeck coefficient, σ is electrical conductivity, T is temperature, and κ is thermal conductivity. To enhance thermoelectric conversion efficiency, the material must exhibit a high S_e, excellent σ, and low κ. However, achieving all these properties simultaneously in a single material remains a significant challenge. To establish an ideal reaction mechanism and molecular design guidelines, it is crucial to observe the reaction field. However, X-ray structural analysis of fluids, particularly liquids, is challenging and remains largely unexplored. In this study, we identified the redox pair quinone/hydroquinone in sodium chloride solution under flow conditions.

The functional group discrimination of quinone/hydroquinone in aqueous NaCl solution was investigated by measuring carbon (C) *K*-edge X-ray absorption spectroscopy (XAS) spectra. The XAS measuremnt was conducted at BL3U of UVSOR equipped with a transmission liquid flow cell [2]. The energy range was set to 280–300 eV, with grating widths of 129 μm/61 μm (S_0/S_1). A 100 mM NaCl solution served as the standard (baseline) sample, to which 10 mM quinone and hydroquinone were added, respectively. The XAS spectra were analyzed based on Lambert-Beer's law as following:

$$\mu t = \ln \frac{I_0}{I_1} \quad (2)$$

where μ is absorption coefficients, t is sample thickness, and I_0 and I_1 represent the incident and transmitted light intensities, respectively. The XAS spectra of 10 mM quinone/hydroquinone in aqueous NaCl solution were applied baseline correction using those of the 100 mM NaCl solution.

The peaks observed at 285.9 eV and 293.0 eV correspond to C1s–π* of C=C and C1s–σ* of C=C resonances, respectively (Fig. 1), indicating their origin from the six-membered rings of quinone and hydroquinone. The intense peak at 288.4 eV corresponds to a C1s–π* of C=O resonance (Fig. 1), suggesting its association with the quinone functional group. These findings confirm the detection of quinone and hydroquinone signatures in the spectrum, demonstrating that their functional groups can be observed in the fluid phase.

Future studies will use electrochemical measurements and XAS analysis at BL3U to further clarify the redox mechanism in TECs with quinone-based systems. Solvation by redox species and solvents is crucial for TEC performance. To explore solvation effects, including hydrogen bonding, *operando* soft X-ray XAS will be conducted on solutions with dissolved redox species. We will examine how solvation influences redox behavior under different solvent compositions, acidity levels, and electrolyte concentrations. These insights will aid in optimizing thermochemical energy conversion systems.

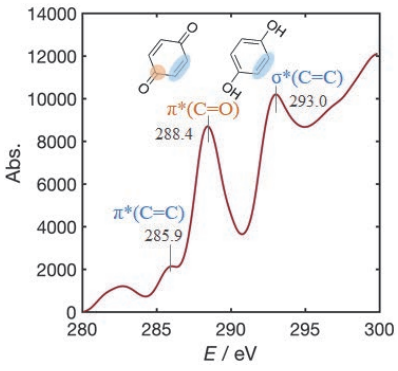

Fig. 1. C *K*-edge XAS spectra of 10 mM quinone/hydroquinone in 100 mM NaCl solution.

[1] H. Zhou *et al*., Angew. Chem. Int. Ed. **62** (2023) e202213449.

[2] M. Nagasaka *et al*., Chem. Lett. **50** (2021) 956.

III-3

BL3U

The Electronic States of 1-Methylimidazole in the Acetic Acid/1- Methylimidazole Mixture

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We have observed the electronic structure of acetic acid and 1-methylimidazole (1-MI) molecules in their solution by soft X-ray spectroscopy to investigate the cause of the change in electrical conductivity of 1- MI/ acetic acid mixtures [1, 2]. The electrical conductivity of the solutions changes drastically when the mixing ratio is changed, with maxima at mole fractions of acetic acid (χ_{AcO}) of 0.65 and 0.85. The results of previous analyses showed that the ionic content of acetic acid and 1-MI was maximum around $\chi_{AcO} = 0.70$, while the ionic content decreased at concentrations of $\chi_{AcO} = 0.85$. The reason why the electrical conductivity reaches a maximum value at the high acetic acid concentration, despite the decreasing amount of ions, is thought to be due not only to the diffusion of the ionic molecules (acetic acid ions and 1-MI ions) themselves, but also to the proton hopping between the acetic acid monomers and 1-MI or through acetic acid chain clusters. However, the previous measurements have only been made to analyze the molecular species in the mixed solution under steady-state conditions. Since an electric field is applied to the solution when electrical conduction occurs, the application of an electric field generates acetate ions that do not exist under steady-state conditions, and the possibility of an increase in electrical conductivity due to the diffusion of these ions was considered. In this experiment, the electronic state of acetic acid molecules in the mixed solution was observed in an electrochemical cell during the application of an electric field to confirm whether new ions were generated.

Soft X-ray absorption spectroscopy measurements at the O K-edge were performed using a transmission electrochemical cell for the solution. Fig. 1 and 2 show the absorption spectra of acetic acid at $\chi_{AcO} = 0.70$ and 0.85 with and without the application of an electric field. As 1-MI dose not contain any oxygen atoms, the absorption spectra at the O K-edge only reflect information about the acetic acid molecules. Previous studies have shown that absorption peaks originating from the $O_{C=O}$ $1s \rightarrow \pi^*_{OCO}$ and O_{OH} $1s \rightarrow \pi^*_{OCO}$ transitions appear at around 532.6 eV and 535 eV for molecules containing the COOH group. When the carboxy group ionises to COO^-, the two oxygen atoms become chemically equivalent, the positions of the two absorption peaks coincide and the second peak no longer appears [1]. In other words, as the acetate neutral molecules in solution become acetate ions, or as more acetate ions come close to the electrode surface, the intensity of the second peak is expected to decrease as the overall spectral shape. Figure 1 shows that the intensity of the second peak was 0.50 relative to the first peak without the application of an electric field, while the intensity of the second peak was 0.36 when an electric field of 0.7 V was applied, indicating a clear decrease in the intensity of the second peak. However, no effect of the electric field application was observed for the solution with mole fraction $\chi_{AcO} = 0.85$, and it was experimentally confirmed that the application of the electric field caused the formation of acetate ions and that the increase in conductivity due to the increase in ion content was unlikely to have occurred. This result supports the idea that proton hopping is the cause of the increase in conductivity in the solution with mole fraction $\chi_{AcO} \sim 0.85$.

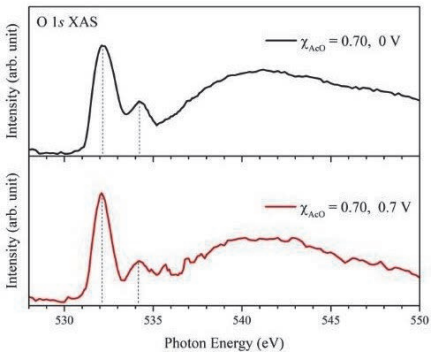

Fig. 1. O K-edge X-ray absorption spectra of acetic acid in the solution of $\chi_{AcO} = 0.70$ with and without the application of an electric field.

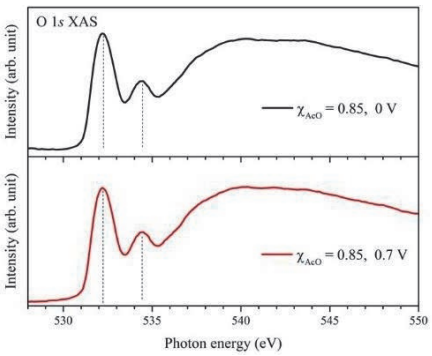

Fig. 2. O K-edge X-ray absorption spectra of acetic acid in the solution of $\chi_{AcO} = 0.85$.

[1] N. Yoshimura *et al*., J. Phys. Chem. B **123** (2019) 1332.

[2] Y. Horikawa, M. Okazaki and M. Nagasaka, UVSOR Activity Report **51** (2023) 129.

BL3U

Oxygen K-Edge XAS-Evidenced Specific Hydrogen-Bonded Water inside Hydrophobic Single-Walled Carbon Nanotubes

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[1]*Research Initiative for Supra-Materials Shinshu University, Nagano 380-8553, Japan*
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Understanding the properties of hydrogen-bonded water molecules around functional groups on nanopores of hydrophobic carbon surfaces or biological substances is crucial. Although presence of only trace amounts of water molecules around functional groups on the hydrophobic surfaces are presumed, their effects should dominate the important phenomena such as water/ion permeation and energy storage in the electrical double layer [1, 2]. The direct observation of the hydrogen-bonded structure of only slight amount of water molecules inside nanopores is very challenging with conventional diffraction technique or Raman/IR spectroscopy because the background of solid hinder the signals of trace amount of water molecules. However, X-ray absorption spectroscopy (XAS) is a powerful tool for investigating the hydrogen-bonded structure of only a tiny water molecules inside nanopores, as it selectively detects specific atoms of interest [3]. In this study, we applied XAS to water molecules inside highly hydrophobic single-walled carbon nanotubes (SWCNTs). SWCNT has well-defined hydrophobic cylindrical nanopores, enabling to investigate the interactions between trace amount of water molecules and isolated functional groups on the graphene wall.

SWCNT with a diameter of 2 nm were purified by heating at 2073 K in vacuo for 3 hours, removing most of impurities. End-caps were removed by air oxidation at 823 K, enabling water molecules to access the SWCNT internal pores. The SWCNTs were dispersed in EtOH at a concentration of 0.01 wt%, and the dispersion was casted onto a SiN membrane with a thickness of 100 nm. EtOH were removed by vacuum evaporation at room temperature, producing a thin SWCNTs film with a thickness of 3 μm on the SiN membrane. The SWCNTs film on the SiN were placed in a XAS measurement chamber. O K-edge XAS spectrum of SWCNTs were measured in the range of 525 – 550 eV under water vapor introduced into the chamber via He bubbling of pure water.

Figure 1 shows the water adsorption isotherm of the SWCNTs. At the relative pressure (P/P_0) below 0.65, the water adsorbed amount is very small, suggesting the water exists as isolated water clusters inside SWCNT [4]. We carried out XAS measurement at $P/P_0 = 0.5$, where the water adsorbed amount is 20 mg g^{-1}, being only 4 % of the fractional filling against saturated adsorbed amount.

Figure 2 shows Oxygen K-edge XAS spectrum of SWCNTs. At $P/P_0 = 0$, two peaks are observed. A sharp peak at 532 eV and a broad peak at 539 eV are assigned to C=O and C-O, respectively. At $P/P_0 = 0.5$, the sharp peak at 532 eV broadens, evidencing the interactions between C=O and water molecules via hydrogen bonding. Furthermore, the intensity of the broad peak increases in the range of 536 – 542 eV due to the presence of water clusters. The increase of the broad peak intensity suggests that the intermolecular distance of water molecules fluctuates from the equilibrium distances. This is the direct evidence on water-surface oxygen groups interactions inside highly hydrophobic carbon spaces.

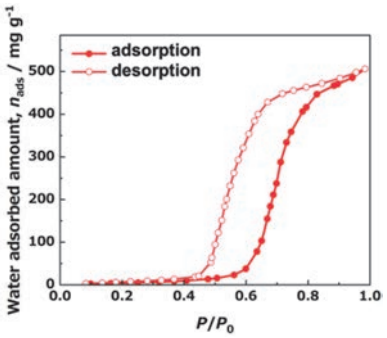

Fig. 1. Water adsorption isotherm of SWCNT at 298 K.

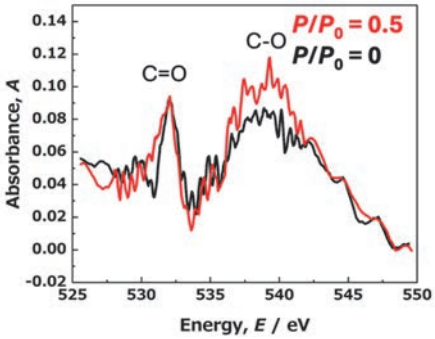

Fig. 2. O K-edge XAS spectrum of SWCNT.

[1] D. A. Doyle *et al.*, Science **280** (1998) 69.
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[3] T. Fransson *et al.*, Chem. Rev. **116** (2016) 7551.
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III-4

BL3U

Ionic Layers at the Electrode Interface of Ionic Liquids Studied Using Interface-Selective Soft X-ray Absorption Spectroscopy

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Ionic liquids (ILs), which are entirely composed of cations and anions, are appealing materials as electrolytes for energy devices. In such devices, the electrochemical interface between ILs and electrodes is an electrochemical reaction field that strongly influences the local reaction rate and thereby the net ones such as charging speed for batteries. Thus, it is of crucial importance to study, and further control, the interfacial structure of ILs at the electrode interface. In the present study, we adopted soft X-ray absorption spectroscopy (XAS) to reveal the interfacial structure of ILs at the electrode interface in an interface-selective manner [1].

1-Butyl-1-methylpyrrolidinium bis(fluorosulfonyl) amide ([C4mpy$^+$][FSA$^-$]) that contained Li$^+$[FSA$^-$] at a concentration of 0.5 M was used as IL [2]. *In-situ* XAS measurements for the IL/electrode interface were performed at BL3U at UVSOR-III, by using an electrochemical liquid flow cell [1]. The IL was sandwiched with two SiC membranes in the He-filled chamber and XA spectra were measured in transmission mode for the nitrogen, oxygen, and fluorine K-edge regions. The photon energy was calibrated by the first peak in the nitrogen or oxygen K-edge region for a ProLINE polymer thin film in a vacuum chamber [3]. The thickness of the IL film was controlled with the He pressure [4]. The platinum film deposited at the inner surface of one of the two SiC membranes was used as the working electrode. Pt wires, as the quasi-reference and counter electrodes, were located aside the film region inside the electrochemical cell. The potential of the working electrode with respect to the quasi-reference electrode was controlled using a potentiostat.

Figure 1 shows fluorine K-edge XA spectra for the IL/platinum interface at three different potentials. At 0 V (black dashed line), where no IL-ion accumulation/depletion occurs at the interface and therefore the interfacial structure corresponds to the bulk one, double sharp peaks were discernible at the absorption edge around 688 and 692 eV, both of which originate from FSA$^-$, according to a prediction using the GSCF3 code for inner-shell excitation [5]. When negative potentials were applied at the IL/platinum interface, the XA spectra (Fig.1, blue and green lines) showed three potential-dependent features. First, the lowest-energy peak decreased in intensity and blue-shifted. Second, the second lowest-energy peak was broadened. Third, the intensity at the high-energy region became higher. These three features demonstrate that the present XAS measurements in transmission mode with a nm-scale thin film setup sensitively detect the interfacial structure, which is different from the bulk one and is also potential-dependent. Oxygen and nitrogen K-edge XA spectra (data not shown) exhibited similar potential-dependent features, although the behavior for the lowest-energy peak was element-dependent. Furthermore, the oxygen K-edge spectra at negative potentials showed an evolution of pre-edge peak, which clearly indicates the formation of solid electrolyte interphase (SEI). SEI, which is indispensable for a stable battery anode and therefore has been extensively studied, is generally difficult to investigate in an *in-situ* manner, illustrating the powerfulness of the present *in-situ* XAS method. The SEI formation is highly likely to cause the intensity increases at the high-energy region observed for all three elements, as exemplified in Fig.1 for the fluorine case.

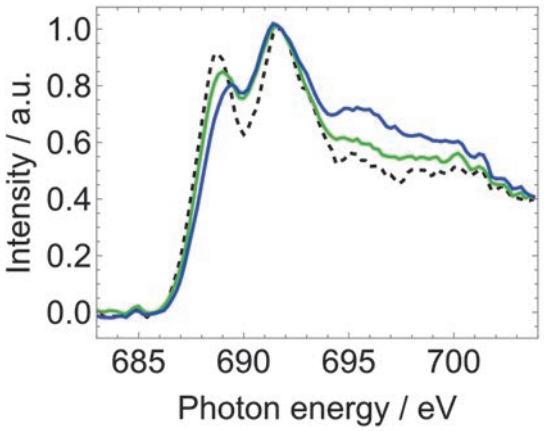

Fig. 1. Fluorine K-edge XA spectra for the IL/platinum interface at 0 (black dashed), −2 (green), and −2.5 V (blue).

[1] M. Nagasaka *et al.*, Rev. Sci. Instrum. **85** (2014) 104105.
[2] S. Kato *et al.*, J. Electrochem. Soc. **169** (2022) 076509.
[3] M. Nagasaka *et al.*, J. Electron Spectrosc. Relat. Phenom. **224** (2018) 93.
[4] M. Nagasaka *et al.*, J. Electron Spectrosc. Relat. Phenom. **117** (2010) 130.
[5] N. Kosugi, Theor. Chim. Acta **72** (1987) 149.

BL3U

Cation-Specific Effects on Interfacial Water Structure Around Silica Nanoparticles Probed by O K-edge NEXAFS

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Understanding the interfacial water structure at the nanoparticle-electrolyte interface is essential for advancing applications in catalysis, separation science, environmental remediation, and biomedicine. Silica nanoparticles (SiO_2), which develop surface charge through silanol group deprotonation, offer a model system for such studies. The organization of water around these charged particles—strongly influenced by particle size, shape, concentration, and particularly the type of counterion, remains poorly resolved, especially at the nanoscale [1].

In this beamtime at the BL3U beamline (UVSOR-III), we investigated cation-specific effects on interfacial water structures in colloidal dispersions of silica nanoparticles using oxygen K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. In this preliminary study, nanoparticles (8-10 nm) were suspended in aqueous media with Na^+ as the stabilizing counterion at various concentrations (10-30 wt%). The experiment builds on recent studies showing interfacial water perturbations induced by nanodiamond surfaces [2] and is a precursor to planned systematic studies involving a full alkali series (Li^+, Na^+, K^+, Rb^+, Cs^+).

Measurements were performed in a liquid flow cell configuration, where liquid samples were sandwiched between two 100 nm thick Si_3N_4 membranes (window area: 2 × 2 mm²) with 100 µm Teflon spacers. Liquid exchange was achieved in situ via tubing pump, with temperature controlled at ~25°C. A 200 × 200 µm² beam spot was selected to optimize photon flux.

Oxygen K-edge NEXAFS spectra were collected and analyzed to investigate the characteristic spectral features corresponding to different water environments: the pre-edge (~535 eV), main-edge (~537 eV), and post-edge (~540 eV), as shown in Fig. 1. These features provide insight into the electronic structure and hydrogen bonding states of water molecules near nanoparticle surfaces. To correct for potential variations in liquid film thickness and to enable direct comparison across different conditions, the spectra were normalized either to the intensity at the pre-edge or post-edge region.

In this study, the SiO_2 nanoparticle concentration was fixed at 15 wt%, and the key variable was the type of dissolved cation—Li^+, Na^+, K^+, Cs^+, NH_4^+, as well as multivalent anion-containing salts like Na_2SO_4 and K_2SO_4. Despite the constant nanoparticle loading, the post-edge intensities exhibited noticeable variation depending on the cation present. In general, larger or less strongly hydrated cations (e.g., Cs^+, NH_4^+) led to enhanced post-edge features, which suggests a more ordered or polarized water structure at the nanoparticle interface. This may be attributed to differences in ion hydration behavior and their impact on the arrangement of water molecules in the electrical double layer.

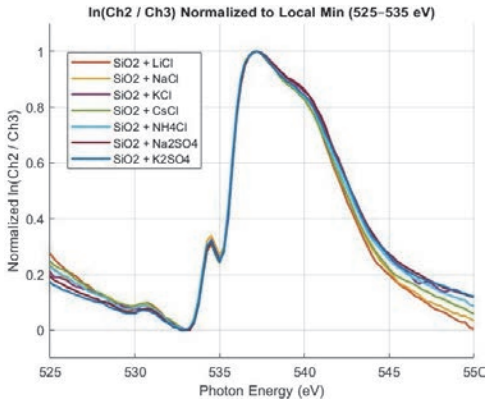

Fig. 1. O K-edge NEXAFS spectra of 15 wt% SiO_2 nanoparticle solutions in the presence of different salts: LiCl, NaCl, KCl, CsCl, NH_4Cl, Na_2SO_4, and K_2SO_4. All measurements were conducted at 25 °C. The spectra have been normalized both to the post-edge maximum and the pre-edge feature to account for differences in sample thickness and to facilitate comparison of spectral features across different ionic conditions.

Conversely, the pre-edge intensity—which reflects contributions from distorted or weakly hydrogen-bonded water species—was found to decrease for certain salts, indicating that specific cations can promote stronger hydrogen bonding or more structured water layers near the surface. These ion-specific trends point to the subtle yet significant influence of cation size, charge density, and hydration enthalpy on interfacial water structuring.

These results are consistent with prior molecular dynamics simulations and spectroscopic studies showing that cation identity modulates interfacial water orientation and hydrogen bonding patterns. The findings reinforce the capability of soft X-ray absorption spectroscopy to sensitively detect changes in interfacial solvent structure induced by ion-specific interactions, even in complex colloidal systems.

[1] Abbas *et al.*, J. Phys. Chem. C **112** (2008) 5715.
[2] T. Petit *et al.*, J. Phys. Chem. Lett. **6** (2015) 2909.

III-4