



Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec



Development and application of *in situ/operando* soft X-ray transmission cells to aqueous solutions and catalytic and electrochemical reactions

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ARTICLE INFO

Article history:

Received 1 March 2015

Received in revised form 19 May 2015

Accepted 19 May 2015

Available online xxx

Keywords:

In situ soft X-ray absorption spectroscopy

Aqueous solution

In operando XAFS

Catalytic reaction

Electrochemical reaction

ABSTRACT

In this review, we have demonstrated several applications of newly-developed *in situ/operando* liquid flow cells for the transmission XAS (X-ray absorption spectroscopy) measurement in the soft X-ray undulator beamline BL3U dedicated to the chemical application of UVSOR-III Synchrotron. The liquid layer is sandwiched between two thin membranes and its thickness is easily controllable to optimize the absorbance. Liquid samples are exchangeable *in situ*. Molecular spectra in liquid and gas phases are simultaneously measurable and it makes the energy calibration rather easy. By using a standard version of the liquid cells, we have investigated local structures of several aqueous solutions of alkali halides, methanol, pyridine, and acetonitrile. To observe catalytic and electrochemical reactions under realistic conditions, we have developed *in situ/operando* versions of the liquid cells. We have investigated local structures of the catalytic hydration reaction of cyanopyrazine under the temperature control and the electrochemical reaction of aqueous iron sulfate solutions using the built-in electrodes under the same scan rate as in cyclic voltammetry. We have discussed future perspectives of our *in situ/operando* liquid flow cells applied to XAS in the soft X-ray region.

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1. Introduction

Macroscopic properties of aqueous solutions, such as viscosity, boiling point, and freezing point, are determined by the interaction between solvent water molecules and solute ions or molecules. In aqueous salt solutions, hydrogen bonding (HB) networks of water molecules are modified or broken by the interactions with solute ions [1–3]. In aqueous methanol solutions, the entropy is smaller than expected in an ideal solution of randomly mixed molecules [4] and shows a nonlinear profile in viscosity at different concentrations [5], indicating some structured interactions between water and methanol molecules. The bond lengths and the coordination numbers of solute ions and molecules with solvent water molecules in aqueous solutions have been extensively studied by neutron diffraction [6–8] and X-ray diffraction [9].

In addition, spectroscopic studies are crucial to reveal the interaction between solvent water molecules and solute ions or

molecules: for example, vibrational spectroscopies such as infrared (IR) and Raman spectroscopies. For example, the OH stretching mode is effectively observed in Raman spectroscopy [10–12] to reveal the hydration structure of the anion to the hydrogen of water in aqueous salt solutions. In aqueous pyridine solutions, the HB interaction between N atoms in pyridine and water molecules is revealed by IR [13] and Raman spectroscopy [14,15]; in aqueous acetonitrile solutions, the HB interaction is revealed by the C≡N and OH stretching modes in IR spectroscopy [9,16,17]. In aqueous methanol solutions, the local structures around methanol molecules at different concentrations are revealed by the C–O stretching modes in Raman spectroscopy [18]. However, vibrational spectroscopy is not enough to understand the local molecular interaction in solutions. For example, the OH stretching mode is not so useful to reveal the hydration structure of the cation to the oxygen of water. Minor components are often hindered by dominant vibrations of solvent molecules with similar wavenumbers. Therefore, the interaction of solutes with solvent water molecules in aqueous solutions should be investigated by combination with other spectroscopies sensitive to the local molecular interaction.

X-ray absorption spectroscopy (XAS) is an element-specific method to study local structures of aqueous solutions. Especially, the soft X-ray region below 1 keV has chemically important

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absorption edges such as C K-edge (280 eV), N K-edge (400 eV), and O K-edge (530 eV). Observation of the L-edge (2p) spectra of 3d transition metals such as Ti L_{III}-edge (460 eV) and Cu L_{III}-edge (930 eV) is important, considering that the L-edge of 3d transition metals is more sensitive than the K-edge to the 3d valence and spin states [19–21]. Recently, the local structures of liquid water have been extensively studied by O K-edge XAS [22–34], where the pre-edge peak (535 eV) corresponds to the transition from the O 1s electron to the '4a₁' unoccupied state, and the behavior of the pre-edge '4a₁' peak reflects the HB interaction effect on a molecular 4a₁ orbital. The temperature dependence of the pre-edge peak is observed to reveal the change in local structure of the HB network in liquid water [25,26,29,31,33,34]. The pre-edge peak in O K-edge XAS of aqueous salt solutions is sensitive to the hydration structure of solute ions (especially, cations) [35–42]. On the other hand, the C and N K-edge XAS can be used to reveal the local structure of solute molecules in aqueous solutions. For example, in aqueous methanol solutions, the hydrophobic interaction of the methyl group in methanol molecule is revealed in the C K-edge XAS [43–45].

XAS is a quite promising method to investigate the local structure of aqueous solutions. XAS spectra of liquid samples can be obtained in transmission mode [30,32–34,46] based on the Lambert–Beer law. XAS-like spectra are measured by fluorescence yields [23,24,26,28], hard X-ray Raman scattering [22,29,31], and total electron yields [25] and inverse partial fluorescence yields [47–49] of microjet liquids. In these alternative methods, comparison with the transmission spectra is discussed as regards background subtraction, normalization, saturation effect, and self-absorption effect, and indicates that XAS-like spectra of bulk liquids measured by hard X-ray Raman scattering and by inverse partial fluorescence yields is nearly the same as XAS spectra in transmission mode. Combination with theoretical simulations of the O K-edge XAS of liquid water is important in revealing its local structure [23,24,26,28,50–56], but should be compared with the true transmission spectrum based on the Lambert–Beer law in the case of quantitative and detailed discussion of spectral features in XAS. However, it is difficult to measure XAS spectra of liquid samples in transmission mode because soft X-rays are strongly absorbed by solvent water beyond the water window region and the thickness of the liquid layer should be kept below a few micrometers [57].

Recently, we have successfully developed some unique liquid flow cells for XAS of liquid samples in transmission mode [30]. The cell is attachable to our IR spectrometer as it is. By using a standard version of liquid flow cells, we have investigated the local structures of several aqueous solutions, such as aqueous salt [42], methanol [45], pyridine [58], and acetonitrile solutions [59]. Furthermore, we have developed *in situ/operando* XAS observation systems to measure the local structural change in catalytic and electrochemical reactions under realistic conditions by extending our liquid cell approach. We have investigated cyanopyrazine (PzCN) hydration reaction to produce pyrazinamide (PzCONH₂) on the TiO₂ catalyst [60] and the change in valence of Fe ions in aqueous iron sulfate solutions from the Fe L-edge XAS spectra [61,62]. In the present review, we describe details of our liquid flow cells for the transmission XAS measurement and several applications to aqueous solutions and catalytic reactions in Section 2 and to electrochemical reactions in Section 3. In Section 4, we summarize the present applications and discuss the future perspectives.

2. Aqueous solutions and catalytic reactions

2.1. In situ liquid flow cell

Fig. 1 shows schematics of the liquid flow cell for XAS in transmission mode [30]. The cell consists of four regions (I), (II), (III),

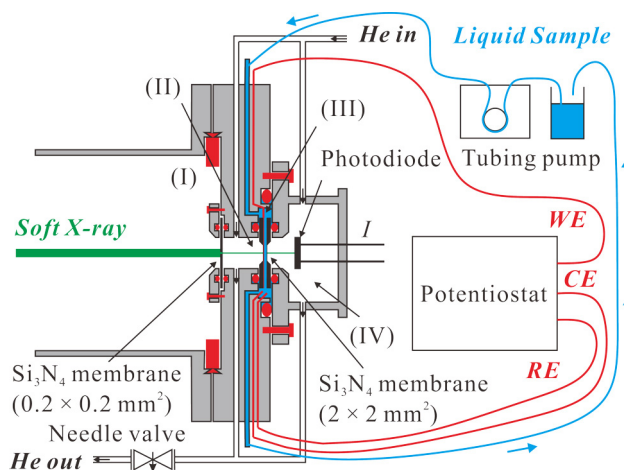


Fig. 1. Schematic of a simple version of the liquid flow cells for XAS in transmission mode [30]. The details of the cell are described in the text. The electrochemical cell will be shown later (Fig. 22). Any liquid flow cell developed in the present work is attachable as it is to IR spectrometers as well as soft X-ray beamlines.

and (IV), separated by 100 nm-thick Si₃N₄ membranes. The Si₃N₄ membrane cannot be used for the N K-edge measurement, but the SiC membrane can be used. Region (I) is connected to the beamline under vacuum. Regions (II) and (IV) are under atmospheric pressure of helium pure gas or mixed gas with reference or other molecules. The size of the Si₃N₄ (SiC) membrane window between regions (I) and (II) is 0.2 mm × 0.2 mm, which is small enough to endure a large difference in pressure, even larger than 1 atm. This orifice determines the size of the soft X-ray beam on the sample. The flow rate of the helium gas in regions (II) and (IV) is changeable by a mass flow controller, and the pressure is adjusted by a needle valve at the gas outlet of regions (II) and (IV).

The thin liquid layer in region (III) is sandwiched between two 100 nm-thick Si₃N₄ membranes with a window size of 2 mm × 2 mm. The liquid flow is under atmospheric condition. Two 100 μm-thick spacers are set between the window frames of the membranes and the frames are compressed by the sealing O-rings to keep the thin liquid layer between the membrane windows below 2000 nm. Liquid samples can be exchanged *in situ* with a tubing pumping system. The temperature of the liquid flow cell can be changed from –5 °C to 75 °C. The thickness of the liquid layer is controllable between 20 nm and 2000 nm by changing the He pressure in regions (II) and (IV).

In order to measure XAS spectra of liquid samples, soft X-rays pass through regions (I), (II), and (III) and are detected by a photodiode in region (IV). The intensity of soft X-rays is normalized by an electric current of a gold mesh in region (I), where the current is proportional to the photon flux. The absorption of soft X-rays in regions (II) and (IV) is small due to the high transmittance of helium [57].

The experiments were performed on the soft X-ray in-vacuum undulator beamline BL3U at UVSOR-III Synchrotron [63]. The XAS spectra are obtained by using the Lambert–Beer formula $\ln(I_0/I)$, in which the transmission signal intensity I_0 is measured for the blank and the transmission signal intensity I is for the liquid sample. The photon energy is calibrated by using the first peak (287.96 eV) of methanol gas [44], the first peak of N 1s → π* band (400.84 eV) of N₂ gas [64], and the O 1s → π* peak top (530.80 eV) of O₂ gas [65], which are mixed with helium gas in regions (II) and (IV).

Fig. 2 shows O K-edge XAS spectra of liquid water at different thicknesses. As shown in the inset of Fig. 2, the thickness of the liquid layer is successfully controlled by adjusting the pressure of the helium buffer gas in regions (II) and (IV). Note that it does not show correct absorption spectra because we did not use energy

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