

Restricted Hydration Structure of Calcium Ion Formed in Slit-Shaped Carbon Micropore

Tomoko Kusudo, Masayasu Nishi, Hiroe Torigoe, Mitsuhiro Ushio, Akira Oda, Yuusuke Sogawa, Atsushi Itadani, Takahiro Ohkubo*, and Yasushige Kuroda
Faculty of Science, Okayama University, Okayama 700-8530, Japan

1 Introduction

We have studied the specific structure of hydrated ions such as Rb^+ confined in solid nanospaces of activated carbons [1, 2] and single-wall carbon nanohorn [3] with the X-ray absorption fine structure (XAFS) technique. The structural information of nano-confined solution (nanosolution; NSN) of metal ions is indispensable for the development of a lot of devices such as electric double layer capacitor. We also understand that a lot of ions such as Ca^{2+} , Cu^{2+} , and Zn^{2+} are playing important roles in our body, and the almost of them can be worked under nano-restricted conditions. Recently, we reported the dehydrated structure around a zinc ion of dissolved zinc acetate [4] and specific structure of dinuclear complex of copper acetate [5] restricted in slit-shaped micropore of activated carbon fiber (ACF). In this report, we will discuss the specific hydration structure around a calcium ion restricted in the micropore of ACF with the data of XAFS spectra and other experimental results.

2 Experiment

In the present study, calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) was impregnated into the micropore of ACF (P7; average pore width = 0.63 nm). The calcium-deposited sample (denoted by P7-Ca) was evacuated at 423 K before the saturated adsorption of water vapor to provide nanosolution formed in the micropore. *In-situ* XAFS measurements were performed at KEK-PF (BL-7C) on the K-edge of Ca (4038 eV).

3 Results and Discussion

Fig. 1 shows the Fourier-transformed spectra of Ca K-edge EXAFS of P7-Ca in evacuated (P7-Ca-evac) and saturated water-vapor adsorbed states (P7-Ca- H_2O), respectively. The figure also shows the spectra of crystal ($\text{Ca}(\text{NO}_3)_2$ -crystal) and aqueous solution of $\text{Ca}(\text{NO}_3)_2$ ($\text{Ca}(\text{NO}_3)_2$ aq.) for comparison. The first shell for each sample can be ascribed to the Ca-O shell. The peak intensity of the first shell for P7-Ca- H_2O is smaller than that of bulk aqueous solution of $\text{Ca}(\text{NO}_3)_2$ even at the saturated adsorption state of water. Also, the ordered structure over 3.1 Å was vanished in the micropore of P7 although the higher shells can be formed around 3.5 Å for both $\text{Ca}(\text{NO}_3)_2$ -crystal and $\text{Ca}(\text{NO}_3)_2$ aq. This result indicates that even if water molecules adsorb and fill the micropore deposited by the electrolyte, water molecules are hard to hydrate to the nearest neighboring of the ion and to form the ordered structure at the higher shell in the micropore of P7.

Table 1 summarizes the structural parameters obtained by curve fitting of reverse Fourier transforms of 1st neighboring shell of each sample. Coordination number ($N_{\text{Ca-O}}$) of the 1st neighbor around a calcium ion for P7-Ca- H_2O is smaller than that in bulk aqueous solution, indicating the formation of dehydrated structure in the micropore of P7. Also, coordination distance between a calcium ion and nearest oxygen atoms ($r_{\text{Ca-O}}$) is obviously decreased compared with that of both $\text{Ca}(\text{NO}_3)_2$ -crystal and $\text{Ca}(\text{NO}_3)_2$ aq. Generally, ionic radii are smaller if the coordination numbers are decreased. Therefore, the smaller distance for P7-Ca- H_2O strongly indicates a high compression effect in the micropore because the distance is still smaller than that of $\text{Ca}(\text{NO}_3)_2$ -crystal even if the coordination numbers are similar to each other.

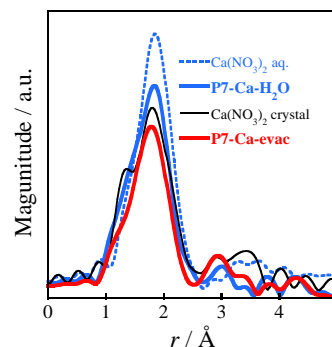


Fig. 1: Fourier-transformed spectra of Ca K-edge EXAFS.

Table 1: Structural parameters obtained by curve fitting.

Sample	$N_{\text{Ca-O}}$	$r_{\text{Ca-O}}/\text{Å}$	$\sigma^2/10^2$ Å^2	$\Delta E/\text{eV}$
P7-Ca-evac	5.6	2.38	0.720	-8.5
P7-Ca-H_2O	7.5	2.40	1.05	-6.4
$\text{Ca}(\text{NO}_3)_2$ -crystal	7.1	2.44	1.18	-5.2
$\text{Ca}(\text{NO}_3)_2$ aq.	8.0	2.45	1.14	0.5

References

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* ohkubo@okayama-u.ac.jp