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Confined Aqueous Ca Solution in Solid Nanospace of Carbon

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1 Introduction

The information of nano-confined aqueous solution (nanosolution; NSN) is indispensable for the development of a lot of devices such as electric double layer capacitor. Hence, we have conducted studies on NSN involving divalent metal ions such as Zn [1, 2], Cu [3], and Co [4] confined in carbon micropores with the X-ray absorption fine structure (XAFS) technique. Also, the study on nano-confined Ca ion is quite important from the aspects of biochemistry, because a lot of Ca ions in our body can act in various kinds of nano-restricted conditions. In this report, we summarize the specific hydration structure around a calcium ion restricted in the micropore of activated carbon fiber (ACF) with the data of XAFS spectra and other experimental results.

2 Experiment

In the present study, calcium nitrate ($Ca(NO_3)_2$) was impregnated into the micropore of ACF (average pore width = 0.63 nm). The Ca-deposited sample (denoted by ACF-Ca) was evacuated at 423 K before the saturated adsorption of water vapor to provide NSN 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 Ca *K*-edge XANES spectra of NSN and bulk aqueous solution of $Ca(NO_3)_2$. The figure strongly support the similarity of hydration structure formed in the carbon micropore and in bulk aqueous solution. Such a similarity can be supported by the structural parameters obtained by the analysis of EXAFS spectra, as shown in Table 1. Although a clear image of dehydrated Ca ions formed in model micropore whose pore width is less than 1 nm could be observed from a molecular simulation technique [5], our results are not agreed with the simulated results. This is because the pore size of ACF is distributed and Ca ions might adsorb into the micropore whose pore width is larger than the diameter of a hydrated Ca ion. Actually, hydration number around a metal ion confined in larger micropore tend to be increased compared with that in narrower micropore [2].

Fig. 2 shows difference adsorption isotherms of water between ACF and ACF-Ca at 303 K as a function of relative vapor pressure. Here, the difference is shown as total number of water molecules per adsorbed Ca ion. The maximum number of adsorbed water per a Ca ion is about 10.5, indicating formation of 2 hydration shells around each Ca ion. Also, over 70% of hydrated water molecules are in the 1st hydration shell, which is caused by the geometrical limitation in carbon micropores. Our present results suggest that the hydrated structure in higher hydration shells must be different from that in bulk phase, though the 1st hydration shell around a Ca ion confined in the micropore is similar to that in the bulk.

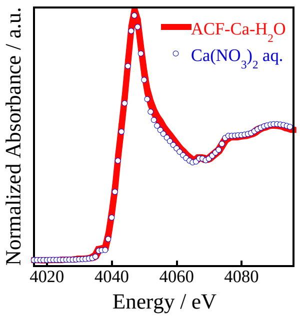

Fig. 1: Ca *K*-edge XANES spectra of nano-confined and bulk aqueous solution of $Ca(NO_3)_2$.

Table 1: Structural parameters obtained by curve fitting.

Sample	$N_{Ca\text{-}O}$	$r_{Ca\text{-}O}$/Å	σ^2/ 10^{-2} Å^2
ACF-Ca-H_2O	7.7	2.42	1.02
$Ca(NO_3)_2$ aq.	7.8	2.43	1.10

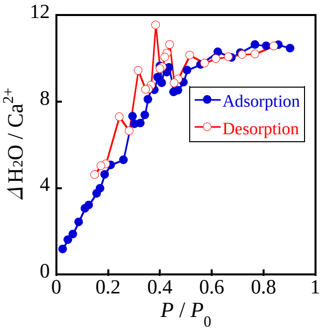

Fig. 2: Difference adsorption isotherms of water between ACF and ACF-Ca at 303 K.

References

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