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Hydration structure around a Zn^{2+} confined in micropores of activated carbons

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Introduction

The local structure around an ion in bulk aqueous solution have been studied and understood by experimental and theoretical techniques. The structural information on ionic solution restricted in nanospaces should provide a new insight for the structure of electrolytic solution[1]. Recently, molecular simulation techniques have been applied to reveal the local structure around an ion confined in the nanospace whose pore width is less than 1 nm[2, 3]. This report summarizes the effect of the pore width on the hydration structure of a Zn ion restricted in carbon nanospaces of activated carbon fiber (ACF)[4].

Experimental

Two kinds of pitch-based ACF (P7 and P20) were used whose average pore-widths are evaluated to be 0.63 and 1.03 nm, respectively. The aqueous solution of zinc acetate ($Zn(OAc)_2$) (0.5 M) were introduced into each ACF followed by washing and drying in desiccator. The $Zn(OAc)_2$-deposited ACF were put on the *in situ* XAFS cell and then the sample was evacuated at 423 K over 2 hours (denoted by P7 or P20-Zn-evac) followed by the adsorption of water to provide the corresponding solution only in the carbon nanospaces (denoted by P7 or P20-Zn-H_2O). XAFS and QXAFS spectra on Zn *K*-edge were obtained and analyzed by IFEFITT and REX2000 codes.

Results and discussion

Figure shows the XANES spectra of P7-Zn-H_2O and P20-Zn-H_2O, respectively. We analyzed the spectra of P7-Zn-H_2O and P20-Zn-H_2O by linear least-square fitting of each spectrum from P7-Zn-evec or P20-Zn-evec with that from bulk aqueous solution of $Zn(OAc)_2$. The ratio of the proportional constants obtained by the fitting can reflect the composition between dissolved and insoluble $Zn(OAc)_2$ inside the micropore. Each fitting spectrum by the linear combination of reference spectra is well agreed with the experimental one, indicating that it is enough for P7-Zn-H_2O or P20-Zn-H_2O to assume only the dissolved and insoluble species. From the fitting analysis, we could estimate the proportion of the dissolved species inside the micropore of P7 and P20 as 21.9 and 36.5 % even at saturated vapor pressure region. These values indicate that the adsorbed water inside the narrower micropore of P7 is hard to penetrate because of the less diffusivity. Here, to estimate the structural information only from the dissolved species in the micropore, we assume that the

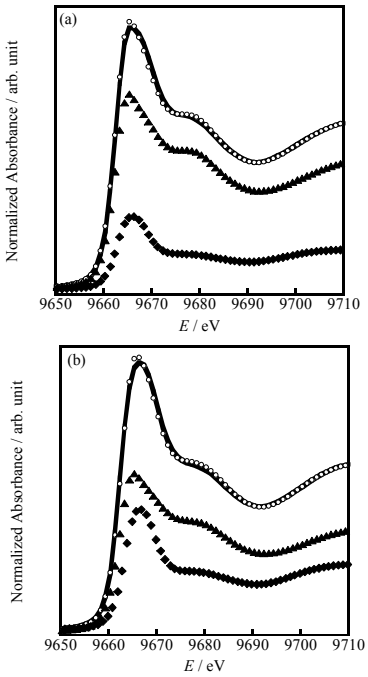

Figure Zn *K*-edge XANES spectra of P7-Zn (a) and P20-Zn(b) at the saturated vapour pressure region of water: experimental data (solid line); evacuated condition (diamond); bulk aqueous solution of $Zn(OAc)_2$ (triangle); sum of the components (open circle).

structural parameters obtained by EXAFS spectra on P7 or P20-Zn-H_2O are the linear combination of dissolved and insoluble species which depends on the proportion of each component obtained by the analysis of XANES spectra. Consequently, the hydration numbers around a Zn^{2+} confined in P7 and P20 are 5.1 and 6.0, respectively[4]. Especially, the hydration number of dissolved species in P7 well sustains the theoretical results showing the moderate dehydration inside less than 1 nm pore[3].

References

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