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Application of a Novel Differential XAFS Approach for Determination of Coordination Geometries

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A novel differential XAFS approach has been developed which allows the determination of small distortions in coordination geometry (distortions in bond lengths and angles) about the absorber. The approach requires taking the difference, $\Delta\chi$, between the XAFS of the sample and a reference material. The Fourier transform of $\Delta\chi$ directly reveals the average of the altered path lengths between the sample and the reference. More importantly, the amplitude of $\Delta\chi$ directly reflects the magnitude of the changes in the bond lengths or angles. FEFF6 calculations verify this approach, and help to interpret the data. Application of this technique has been made to the zincate ion in an alkaline Zn battery, where small distortions from the T_d geometry resulting from ion pair interactions can be determined directly

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1. INTRODUCTION

In general, only the large single scattering (SS) contributions in x-ray absorption fine structure (XAFS) are utilized for determination of the structure of a material. These contributions accurately provide information on the number of atoms and the bond length to the first, and often higher, coordination shell(s) about the absorber. The multiple scattering (MS) contributions can provide even more information, such as the coordination geometry and S-A-S (scatterer-absorber-scatterer) bond angles. The full potential of XAFS has generally not been realized because these MS contributions are often masked by the larger SS contributions and their phase and amplitude satellites, or by the many other MS contributions. In this work, we have developed a novel differential XAFS approach which under certain circumstances allows the isolation of the critical MS contributions so that they can be utilized to provide a determination of small distortions in coordination geometry (distortions in bond lengths and angles) about the absorber.

2. RESULTS

The method depends on taking the difference between the XAFS of the sample and a similar reference material. Assuming $\mu = \mu_0(1+\chi)$, we remove the "background" μ_o utilizing an iterative spline technique [1]. Then the method can be simply simulated by the expression

$$\Delta\chi = A_1 \sin\phi_1 - A_2 \sin\phi_2 = (A_a+\delta A)\sin(\phi_a+\delta\phi) - (A_a-\delta A)\sin(\phi_a-\delta\phi) \quad (1)$$

where $A_a = (A_1+A_2)/2$, $\phi_a = (\phi_1+\phi_2)/2$ and $\delta A = (A_1-A_2)/2$, $\delta\phi = (\phi_1-\phi_2)/2$. Using simple trigonometric relations, (1) reduces to

$$\Delta\chi = 2\delta A\cos\delta\phi \sin\phi_a + 2A_a\sin\delta\phi \cos\phi_a \approx 2A_a [(\delta A/A_a)\sin\phi_a + \delta\phi\cos\phi_a] = 2A_a B \sin(\phi_a+\alpha), \quad (2)$$

where $B = \mathrm{sqrt}[(\delta A/A)^2 + (\delta\phi)^2]$ and $\alpha = \tan^{-1}[A\delta\phi/\delta A]$. The latter two expressions in Eq. (2) are valid only for small $\delta\phi$. To first order $\delta\phi = k\Delta R$ and $\delta A/A = k^2\Delta\sigma^2$ revealing that the amplitude of $\Delta\chi$ is directly proportional to the change in the path length ΔR or the Debye Waller factor, $\Delta\sigma^2$.

As an application of this approach, we consider the Zn K-edge XAFS spectra for zincate ion in solution prepared at 0.75 M in ZnO and 8.4 M in MOH where M is either Li, Na, K, or Rb [2]. Each experimental XAFS spectrum was normalized at 50 eV and slight energy differences believed to be due to monochromator resolution were taken out. Figure 1 shows a comparison of the amplitude of the Fourier transform of the $k^2\chi$ function obtained in the normal fashion for ZnO/NaOH with that obtained in the "differential" technique which involves the Fourier transform of the difference, $k^2\Delta\chi$, between ZnO in NaOH minus that for the reference, ZnO in RbOH. These later two spectra are slightly different because of the ion-pair interaction between the tetrahedral $Zn(OH)_4^{2-}$ ion and two hydrated cations $M^+(H_2O)_x$ (M = Na or Rb), as shown in Fig. 2. Thus $k^2\Delta\chi$ is non-zero because of the weak hydrogen bonds existing between the OH groups on the zincate ion and the water in the hydrated cation, which can cause distortion of the tetrahedral zincate symmetry. In instances where only the bond angles change, the single scattering path contributions (here the Zn-OH path) nearly cancel along with the phase and amplitude satellite peaks. Further the many MS contributions arising from paths which did not change also cancel, allowing

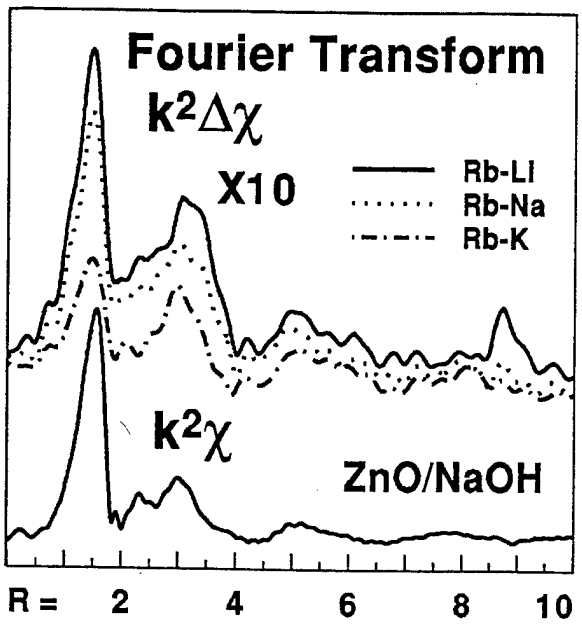

Figure 1. Comparison of the Fourier transform of $k^2\chi$ for ZnO in NaOH with $k^2\Delta\chi$ for RbOH-MOH.

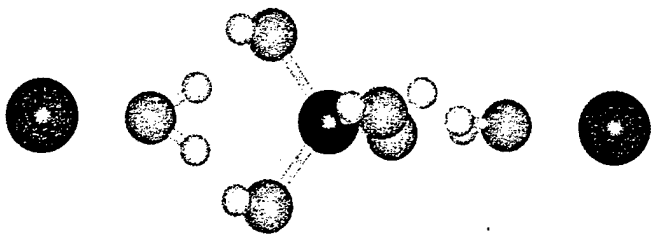

Figure 2: $Zn(OH)_4^{2-}$-$[H_2O$-$M^+]_2$ ion pair interaction model. Spheres in order of increasing size are H, O, Zn, and M^+.

isolation of the critical double and triple scattering paths [e.g., ZnO_2,(the triangular path from Zn to one OH to a neighboring OH back to the Zn] and Zn-O-M [a co-linear path from the O in the water of hydration to the metal cation and return via a 2, 3 ,or 4 step scattering path]. Since the first path necessarily traverses the O-Zn-O angle, the changes in the tetrahedral symmetry (geometries) resulting from the ion-ion interaction can be directly determined. In general, when one of the bond lengths changes relative to the reference, single scattering paths may dominate; but only for the bond length which changed.

Figure 1 clearly shows that the amplitude of nearly all of the peaks in $k^2\Delta\chi$ increase with the size of the cation, indicating that the strength of the hydrogen bonding increases with surface charge density on the metal cation, i.e. the smaller cations (e.g., Li^+) are able to "snuggle" in more closely to the zincate ion. Direct non-linear least squares fitting to these peaks in R-space utilizing phase and amplitude parameters from FEFF6 calculations [3] indicates that the normal tetrahedral zincate ion is increasingly distorted as the cation radius decreases, with the total distortion for Li being larger than 10°. The Zn - OH_2 distance remains relatively constant at 3A° (it is dictated by the more covalent OH-OH_2 hydrogen bond) and the Zn-M distance increases with cation size from 5 to 6A° (Li to Rb), as expected consistent with the ionic radius of the metal ion.

Zinc is a commonly used battery electrode, and zinc primary batteries have found numerous applications. The problem associated with the Zn electrode is its short and unpredictable life time associated with the precipitation of ZnO from the electrolyte[4]. This ZnO precipitate causes the effective mass loss of Zn, reduces electrical contact between the electrode and electrolyte, and eventually destroys battery life. The addition of Li^+ proves to be an effective method to prolonging electrode life time by preventing ZnO precipitation. However there is little understanding of how the Li ion does this [5]. The results here give direct evidence that the smaller hydrated cations form a stronger complex with the zincate ion. We believe this complex formation also occurs at the ends of the polymer chains, thus either stabilizing the $Zn(OH)_2$ chains, or preventing further agglomeration of the ZnO chains. It is found from practical experience that optimal concentrations of Li already occur at Li/Zn = 1/25 [5]. This strongly indicates to us that what is important is the stabilization of the ends of the polymer chains, since we do not believe that one Li ion could keep 25 zincate ions from polymerizing. This polymerization is reversible as long as complete agglomeration to ZnO precipitates is prevented.

Acknowledgments

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