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Atomic Effects in EXAFS Structural Analysis of Redox I^-/I_3^- Solid State Electrolytes†

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Abstract

A highly disordered iodine neighborhood in silica-based nanocomposite redox I^-/I_3^- electrolytes produces a weak EXAFS (Extended X-Ray Absorption Fine Structure) signal at the iodine K-edge. The signal is comparable in amplitude to sharp features arising from intra-atomic effects, the multielectron photoexcitations of the iodine atom. Using pure atomic absorption of neighbor elements, structural and atomic components of the signal are separated and characterized. The iodine atomic absorption background is transferable to EXAFS spectra of other iodine compounds and can be used to minimize systematic error of background removal in structural analysis. The spectral features of the iodine atomic absorption background are found to follow smoothly the trends exhibited by data on the two subsequent elements Xe and Cs.

Key words: EXAFS, multielectron photoexcitations, iodine K-edge.

Introduction

Silica-based nanocomposite redox electrolytes with semi-solid state consistency are used in dye-sensitized photochemical cells and hybrid electrochromic cells. The electrolytes are based on a bis end-capped triethoxysilane precursor chemically bonded via the urea groups to a long poly(propyleneglycol) chain (ICS-PPG 4000 for short).[1-4] Redox conductivity is attained by incorporating KI and I_2 in the sulfolane solution of the ICS-PPG 4000 precursor before gelling with the addition of the acetic acid or salicylic acid. EXAFS (Extended x-ray absorption fine structure) analysis [5] of the iodine K-edge spectra is a method of choice to investigate the sites of iodine atoms in the sol-gel host including a possible association of iodine ions to polyiodide chains. In view of the highly disordered neighborhood of the investigated atoms, the samples produce a very weak EXAFS signal, comparable in amplitude to sharp features arising from intra-atomic effects, the multielectron photoexcitations of the atom.[6-8] Thus, an essential part of the study is a separation of structural and atomic components of the measured signal and comparison of the extracted atomic effects in iodine with pure atomic absorption of neighbor elements Cs and Xe.

Experiment

Four samples were prepared as combinations of two synthesis routes (gelling acid: A = acetic, B = salicylic) and two KI/I_2 molar ratios (V = 20, M = 10). Standard iodine K-edge EXAFS spectra were recorded at the X1 beamline of the synchrotron laboratory Hasylab at DESY, Hamburg, Germany, using a Si 311 double crystal monochromator with energy resolution of ~7 eV at 33 keV (small in comparison to the iodine K vacancy natural width of ~11 eV). High-quality absorption spectra with the edge jump of ~1 and noise level ~5.10^{-5} were obtained. They were analyzed with UWXAFS program package using FEFF6 code for ab initio calculation of scattering paths.[9,10]

Results and discussion

X-ray absorption is basically an atomic process and can be observed as such in monatomic samples: the cross section of the atomic absorption decreases slowly with the energy of the incoming photons and increases abruptly at each threshold for excitation of inner atomic shells (x-ray edges). In the vicinity of the edge and in a relatively short energy region beyond the edge (~1 keV), some additional features are recognized.[6,11]

In atoms, embedded in a solid lattice or in a molecule - in contrast to absorption in free atom samples - the absorption above an absorption edge is modulated with a quasi-periodic structural signal due to the scattering of the outgoing photoelectron on the neighbor atoms (EXAFS signal). This signal can be used to determine the surroundings of the target atoms.[5] The structural signal can usually be well separated from atomic background: the atomic signal represents the smooth middle-line for structural oscillations. Short excursions of the atomic signal akin to structural oscillations are usually much weaker and can be neglected - this is a routine presumption of EXAFS analysis.[9] In our samples, however, the structural signal is very weak due to a low degree of order in the iodine neighborhood and the standard presumption may be wrong.[7,8] If that is a case, additional information is needed to extract the structural signal and parameters. Since the strength of atomic effects in iodine absorption has not been studied before we use the data from our study on atomic absorption of the subsequent elements Xe and Cs [11] (Figure 1). The study has shown only moderate changes in the atomic effects for consecutive elements.

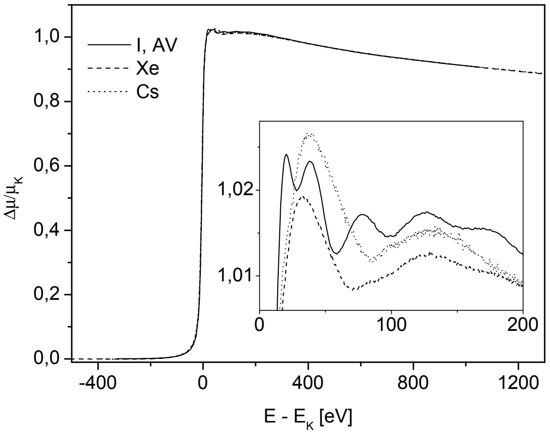

Figure 1. Normalized absorption spectra of iodine in the AV sample, xenon and atomic cesium. Energy scale relative to the respective K edge energy is used for the purpose of comparison (E_K = 33169 eV for I, 34562 eV for Xe and 35985 eV for Cs). Inset: atomic effects and structural signal immediately above the K edge.

The magnified details of Figure 1 in Figure 2 reveal peaks and valleys of the small structural signal in the I spectrum among larger atomic features, similar to those seen in the pure form in Xe and Cs spectra. They occur at the energies where simultaneous excitation of two or more atomic electrons becomes possible – the *multielectron photoexcitation thresholds.* At the threshold an additional contribution to the absorption cross section opens up and saturates in a few tens of eV for the near edge excitations and in a few 100 eV for excitations at the end of the observed energy range. Table 1 gives calculated multiplet intervals of these excitations. The observed onset of a feature in the spectrum can miss by a few eV the calculated interval due to the large natural width. In Xe and Cs spectra the two strong sharp features are the onsets of double 1s4d and 1s3d photoexcitations (in Xe at ~67 eV and ~720 eV). The analogous features hidden in our I spectra mimic structural oscillations and can seriously affect EXAFS analysis. For instance, the amplitude of structural oscillations around 600 eV above K edge is ~2.10^{-4} of the edge jump (Figure 2b), much weaker than the 1s3d atomic feature. In Xe and Cs spectra two smaller sharp features are also visible: the 1s4p double excitation and the triple 1s4d5p excitation (in Xe at ~160 eV and ~100 eV). The cross section for 1s4s excitation is too small to be recognized.

Table 1. Energy intervals of multielectron photoexcitations, calculated in Dirac-Fock model.[12] Values are given in eV, relative to respective K edge energies.

	I	Xe	Cs
1s4d	54-82	76-90	89-104
1s4d5p	78-115	91-137	104-148
1s4p	143-182	162-203	194-236
1s4s	205-235	236-252	260-278
1s3d	665-704	727-754	780-813

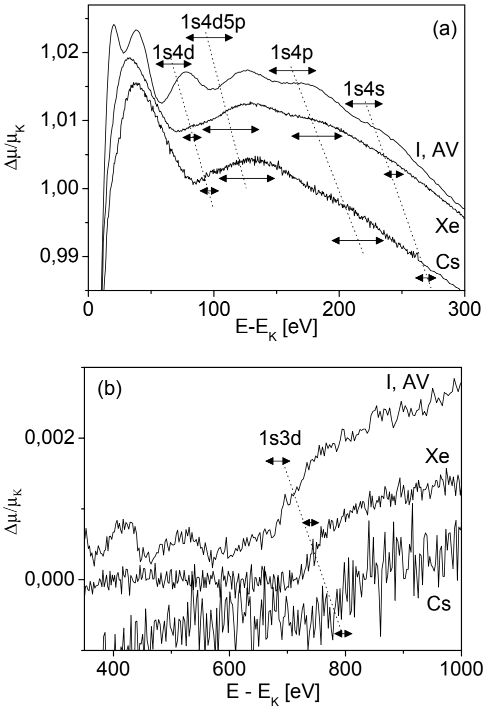

Figure 2. The near (a) and far (b) edge region in I, Xe and Cs K-edge absorption. In (a) Cs spectrum is shifted for -0.011 along vertical axis, in (b) an average downward trend is eliminated and a small vertical shift is introduced for clarity. Intervals of multielectron photoexcitations are shown by arrows.

In the routine EXAFS analysis the oscillating part of the above-edge signal is extracted using a smooth background function in the form of a spline and transformed into wavevector k space (Figure 3). The result for iodine in AV sample looks like an ordinary structural signal but the comparison with Xe and Cs reveals that it is corrupted with atomic effects in the indicated intervals. We can, however, apply EXAFS analysis in the interval between the large 1s4d and 1s3d double excitations, i.e. between 5 and 11 Å^{-1}, neglecting the small corruption by the 1s4d5p, 1s4p and 1s4s features.

Fourier transform of the middle part of the signals (Figure 4) shows only one peak pertaining to the nearest shell of neighbors. Positions of more distant neighbors are disordered and their incoherent contributions cancel out. For characterization of such a simple neighborhood even the short span of useful data defined above is sufficient.

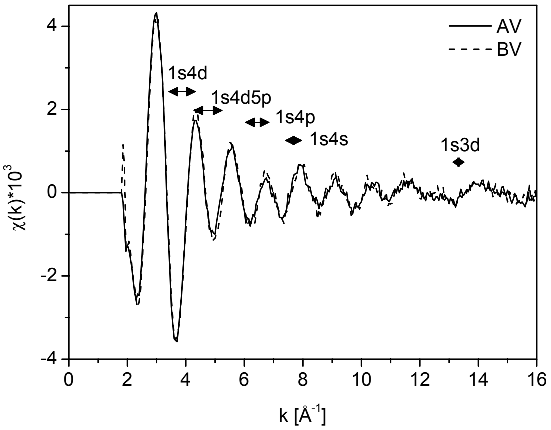

Figure 3. Oscillating part of the above-edge absorption, transformed into electron wavevector scale. Intervals of iodine multielectron photoexcitations (same as in Fig. 2) are shown by arrows.

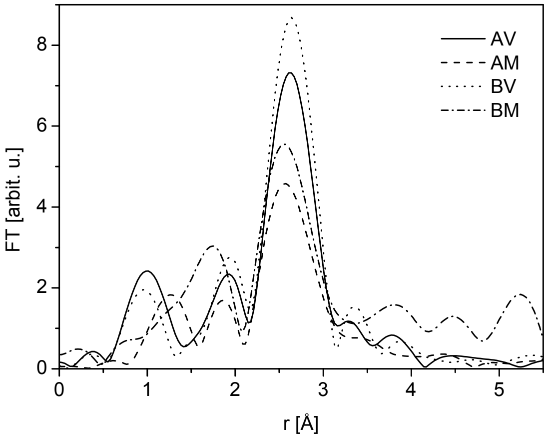

Figure 4. Fourier transforms of the EXAFS signal of four samples show only one peak. The apparent additional structure in BM sample transform is due to a high noise level.

For all samples, the structural signal can be completely described (Figure 5) by a model of I neighbors at ~2.92 Å which is the distance of the terminal I-I bond in iodine chains.[13] It is significantly longer than the nearest-neighbor distance in an iodine crystal or in I_2 molecules (2.70 Å) and significantly shorter than the mid-chain I-I distance (3.14 Å). This indicates that the I chains are short – consisting of 3 atoms.

If all the I atoms in a sample were in 3-atom chains, the average number of I neighbors would be 4/3 (the middle atom has 2 neighbors). We find ~0.4 neighbors in all samples. This means only ~30% of I atoms are associated in chains while the others show no consistent neighborhood.

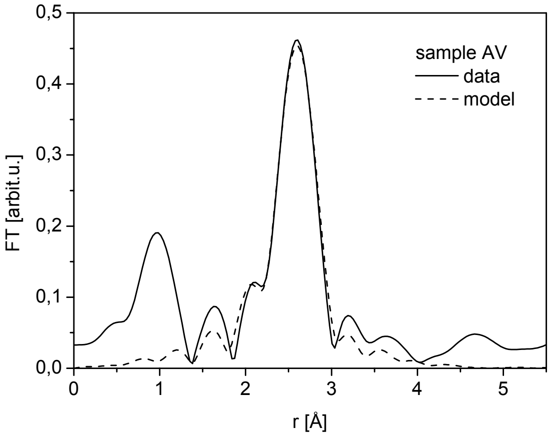

Figure 5. Fourier transform magnitude of the iodine EXAFS spectrum measured on the AV sample together with best-fit structural model. The unphysical peak at ~1 Å, below the contact distance for a neighbor atom, is an artifact of the standard spline background construction.

The four samples differ only in the degree of static disorder in the structure. A larger disorder is recognized from the increased widths, and consequently decreased amplitudes, of the iodine peak in the Fourier transform. It can be expressed by the Debye-Waller factor σ^2. In our samples it varies between 0.008 Å^2 and 0.013 Å^2: more order is found in iodine rich samples and/or samples where salicylic acid was used in the synthesis route.

The structural model obtained from the middle part of the above-edge absorption can be extrapolated to lower and higher energies. In spite of the short spectral region available for the construction of the model, the simplicity of the structural signal assures that no substantial errors are introduced in this procedure. By removing this extended structural model (k = 3–16 Å^{-1} *i.e.* $E-E_K \approx$ 40-1000 eV) from the absorption spectrum, an approximate atomic absorption (*i.e.* atomic absorption background = AAB) [14] of iodine is determined. It is a good approximation of absorption in free iodine atoms and is transferable to EXAFS spectra of other iodine compounds, with the purpose to extract the pure EXAFS signal and thus minimize the systematic error of background removal in structural analysis. In samples with weak structural signal, of which ours was a particularly simple case, the analysis is possible only after the atomic contribution is properly taken into account.

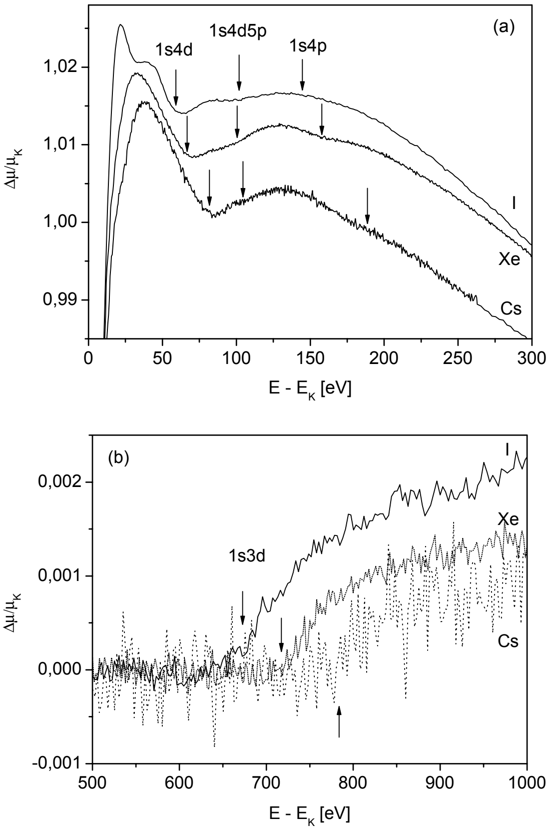

Figure 6. Atomic absorption of I, Xe and Cs - (a) near edge, (b) far K-edge region. Cs spectrum in (a) is shifted for -0.011 along vertical axis for clarity. Onsets of double excitation features are indicated by arrows. Since iodine 1s4p feature is not apparent, the arrow shows the calculated energy.

Figure 6 shows that the extracted iodine AAB is similar to the measured atomic absorption of the two subsequent elements Xe and Cs,[11] confirming the adequacy of the extraction procedure. The onsets of 1s4d, 1s4d5p and 1s3d features are clearly visible (~58 eV, ~99 eV and ~670 eV, respectively); their position agrees well with the calculated energy intervals (Table 1). For 1s4p and 1s4s which lie in the region included in EXAFS modeling the determination is not reliable. The contribution from 1s4s is expected to be negligible on the grounds of comparison with Xe and Cs.

While the positions of the sharp onsets of the double excitation features are rather well defined, determination of their strength is ambiguous since the smooth part of the underlying cross section is also unknown. A reliable estimate can be given only for the 1s3d excitation, lying in a region with monotonous decrease of absorption cross section with energy. In the well studied case of Xe,[11] the total shake amplitude (saturated value) of the 1s3d feature is estimated to ~0.4% of the K edge jump. In I the amplitude is 40% higher giving an estimate of 0.6%.

Conclusions

Due to the specific inclusion of iodine in silica matrix a separation of atomic and structural features in the K-edge absorption data is possible.

Structural oscillations are found to be produced by only one shell of iodine neighbors, their period is characteristic of short iodine chains which contain ~30% of I atoms while the remaining 70% exhibit no systematic neighborhood.

The extracted atomic signal can be used as a good approximation for the atomic absorption background in EXAFS analysis of other I compounds. It is superior to the routine spline construction which is prone to produce artifacts from sharp multielectron spectral features, as seen in Figure 5. The features of the iodine atomic absorption background were found to follow smoothly the trends exhibited by data from the subsequent elements Xe and Cs and predicted by theoretical calculations.

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Povzetek

Močno neurejena okolica joda v redoks I^-/I_3^- elektrolitih, pripravljenih po postopku sol-gel, kaže šibek signal EXAFS (Extended X-Ray Absorption Fine Structure), po amplitudi primerljiv s signalom večelektronskih vzbuditev jodovega atoma. Opisan je postopek, po katerem smo oba signala ločili in ju ovrednotili. T.i. atomsko absorpcijsko ozadje lahko uporabimo tudi pri drugih jodovih spojinah, s čimer zmanjšamo sistematične napake analize EXAFS. Jodovo atomsko absorpcijsko ozadje kaže podobne značilnosti kot atomska absorpcija jodovih naslednikov v periodnem sistemu, ksenona in cezija.