Supporting Information: Ce K edge XAS of ceria-based redox materials under realistic conditions for the two-step solar thermochemical dissociation of water and/or CO_2

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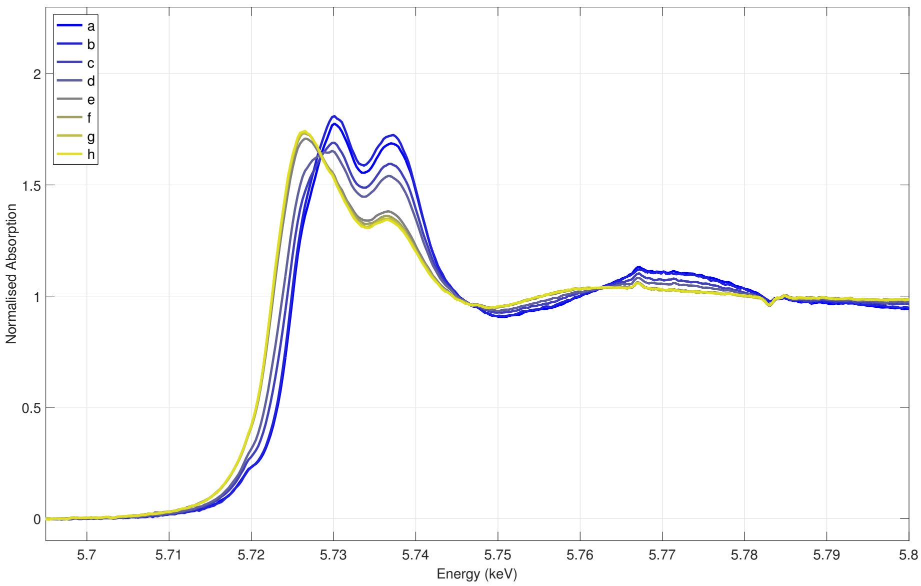
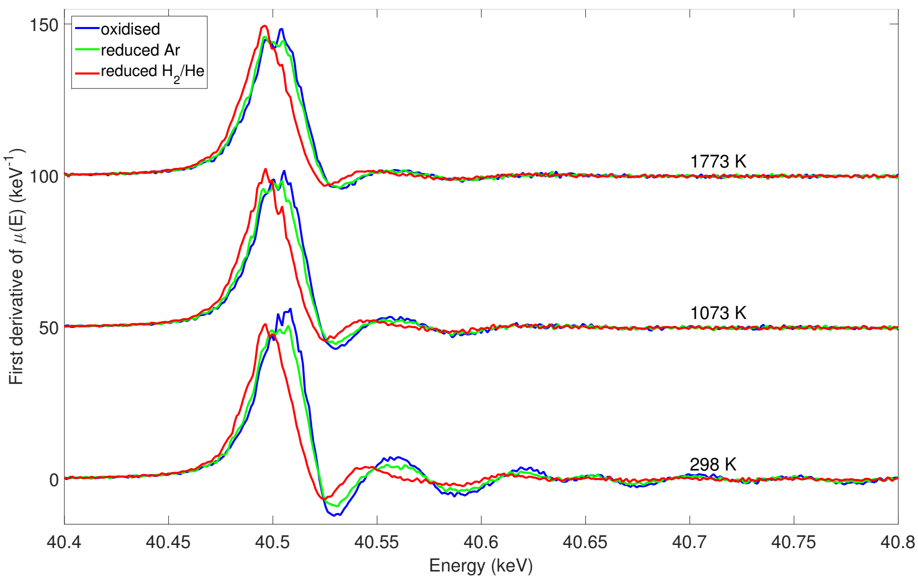
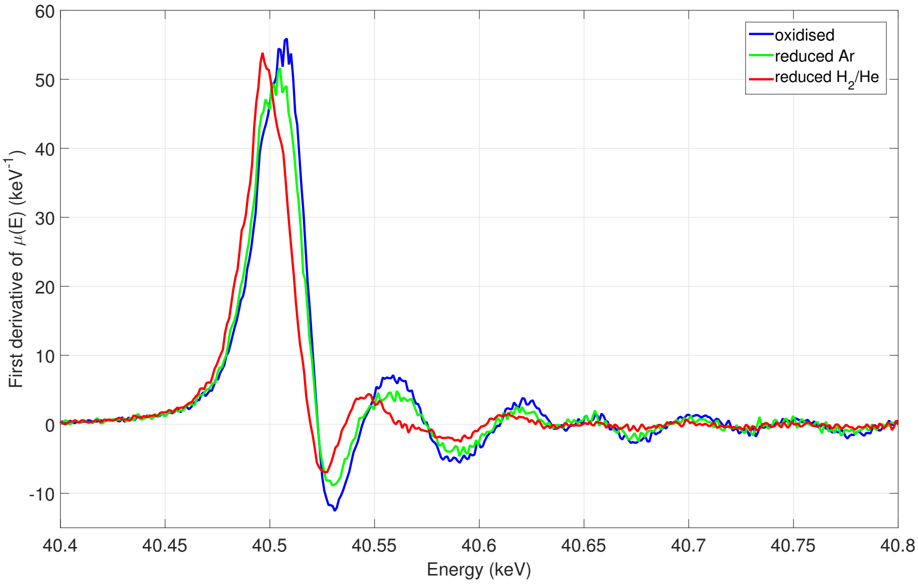


Figure 1: Normalised Ce L_{III} edge absorption spectra recorded during reduction of $Ce_{0.9}Hf_{0.1}O_{2-\delta}$ powder diluted with BN by heating with a rate of 50 Kmin^{-1} from RT (a) to 1073 K (f,g,h) in a flow of helium. Kapton windows were used.

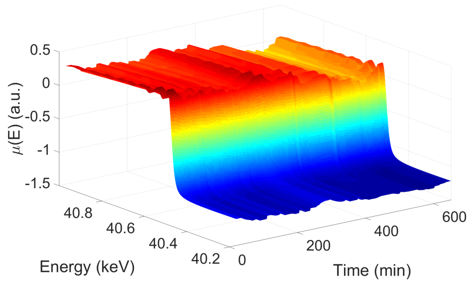


(a)

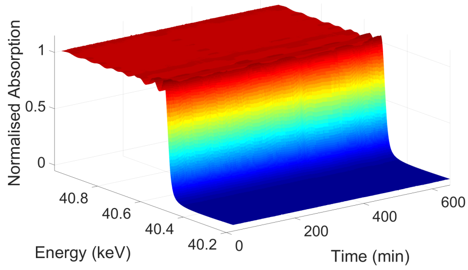


(b)

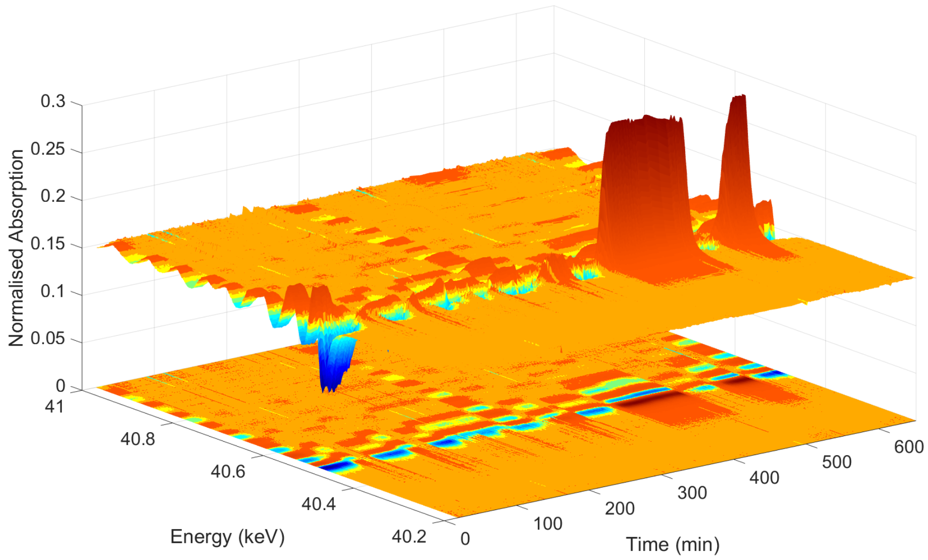
Figure 2: a) First derivative of cerium K edge spectra of $Ce_{0.9}Hf_{0.1}O_{2-\delta}$, recorded at 298, 1073, and 1773 K. 'Oxidised' (298 K) is the spectrum of the as-prepared pellet after introduction into the XAS cell. 'Oxidised' (1073) and 'oxidised' (1773) were recorded after oxidation in 1 atm CO_2. 'Reduced Ar' denotes spectra recorded after reducing the sample in a flow of argon at 1773 K and 'reduced H_2/He' spectra recorded after reducing the sample in a flow of 2% hydrogen/helium at 1773 K. b) Close-up of spectra recorded at 298 K. 'Oxidised' denotes the spectrum of the as-prepared pellet after introduction into the XAS cell. 'Reduced Ar' denotes spectra recorded after reducing the sample in a flow of argon at 1773 K and 'reduced H_2' spectra recorded after reduction in a flow of 2% hydrogen/helium at 1773 K.



(a) Raw Spectra



(b) Normalised Spectra



(c) Difference Spectra

Figure 3: (a) Cerium K edge X-ray absorption spectra, (b) after normalization and (c) difference spectra obtained by subtraction of a spectrum recorded at 1073 K after the first reduction by flushing the reactor with argon at 1773 K.

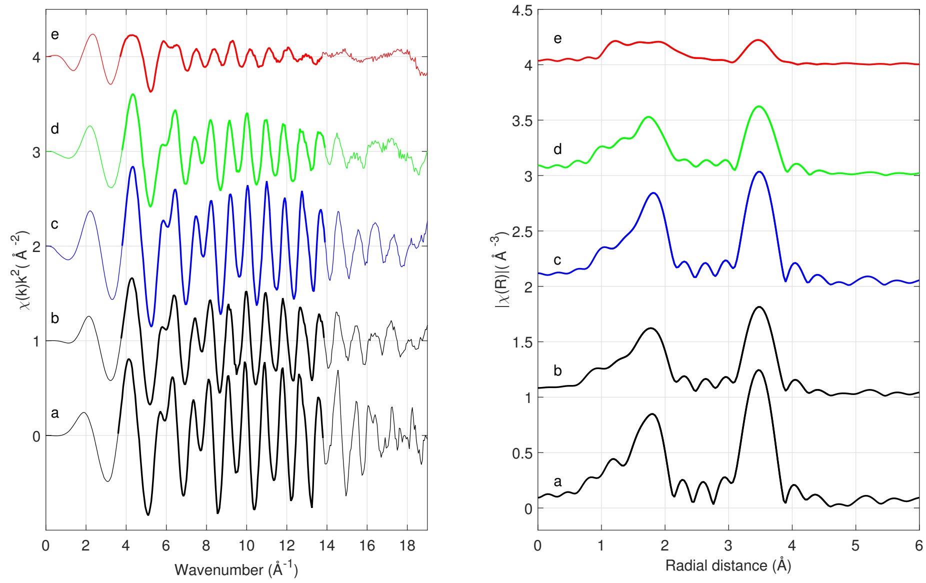


Figure 4: Extended X-ray absorption fine structure (EXAFS) of a) CeO_2 (as prepared) b) $CeO_{1.93}$ (reduced Ar) c) $Ce_{0.9}Hf_{0.1}O_2$ (as prepared) d) $Ce_{0.9}Hf_{0.1}O_{1.92}$ and e) $Ce_{0.9}Hf_{0.1}O_{1.55}$ (reduced H_2) recorded at RT. The bold lines indicate the data range used for Fourier-transformation of $\chi(k)$ to obtain the pseudo-radial distribution functions $\chi(R)$.

1 Energy resolution

At 40 keV, the intrinsic energy resolution of parallel beams reflected on a Si (111) monochromator crystal oriented orthogonally to the polarization plane reported by Sanchez del Rio and Mathon[1] is $\Delta E = 0.135 \cdot 40 = 5.4$ eV. The angular range over which total reflection occurs is described by the Darwin width ω_D of the crystal by the dynamical theory of diffraction. The Darwin width is defined as the full width-at-half-maximum of the reflex of a divergent beam.

$$\omega_D = \frac{2\lambda^2 r_e C\sqrt{|\gamma|}}{\pi V}\frac{|F_{hkl}|}{sin2\theta_B} \tag{1}$$

λ is the photon wavelength, r_e the classical electron radius, C the polarization factor, γ the asymmetric ratio, V the volume of the crystal unit cell, and $|F_{hkl}|$ the structure factor for the selected crystal reflection. For a polarized beam and symmetric Bragg reflection, C and γ are equal to 1.

For Cu K_α radiation with λ=1.54 Å, $\theta_B = 14.22°$, $\omega_{D,Cu} = 3.4 \cdot 10^{-5}$ rad. At high photon energies, the structure factor $|F_{111}|$ can be considered as weakly energy dependent, which extrapolates for $\omega_{D,40}$ to:

$$\omega_{D,40} = \omega_{D,Cu} \cdot \frac{\lambda_{40}^2}{\lambda_{Cu}^2}\frac{sin2\theta_{B,Cu}}{sin2\theta_{B,40}} = 6.6 \cdot 10^{-6} rad \tag{2}$$

A beam with 0.5 mm hight at the sample position located 40 m from the source leads to a divergence $\psi = \frac{0.375mm}{30m} = 1.25 \cdot 10^{-5}$ rad at the monochromator, which is located 30 meters away from the source. In the present case, the divergence ψ is thus about two times as large as the Darwin width.

Considering the intrinsic resolution of the crystal a constant ΔE can be calculated from equation 3: R_T is a measure for the efficiency of the reflection on two crystals and defined as $R_T = R_1 R_2 p_0$, the product the ratios of the source and reflected bandwiths R_1 and R_1 and a coefficient p_0 describing the peak value of the rocking curve.

$$R_T = 1 \cdot \left(\frac{\Delta E}{E}\right)_{intr} \cdot 10^3 \tag{3}$$

According to Table 1 in the work of Sanchez del Rio and Mathon[1] even at $\psi = 5\omega_D$ the value for R_T changes by less than 2%.

$\Delta E_1 = E \cdot R_T \cdot 10^{-3} = 40 \cdot 1346 \cdot 10^{-7} = 5.38$ eV

$\Delta E_{\psi=5\omega_D} = E \cdot R_T \cdot 10^{-3} = 40 \cdot 1373 \cdot 10^{-7} = 5.49$ eV

We can therefore conclude that at 40 keV the energy resolution ΔE of the Si (111) double crystal monochromator with flat crystals is better or equal to 6.0 eV.

References

[1] M. Sanchez del Rio and O. Mathon, *Adv. Comput. methods x-ray neutron Opt.*, 2004, **5536**, 157–164.