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 CO₂

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Figure 1: Normalised Ce $L_{III}$ edge absorption spectra recorded during reduction of Ce$_{0.9}$Hf$_{0.1}$O$_{2-δ}$ 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.
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 reduction 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.
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 is $\Delta E = 0.135 \cdot 40 = 5.4$ eV. The angular range over which total reflection occurs is described by the Darwin width $\omega_D$ 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.

$$\omega_D = \frac{2\lambda^2 r_e C \sqrt{|\gamma|} |F_{hkl}|}{\pi V \sin 2\theta_B}$$  \hspace{1cm} (1)

$\lambda$ is the photon wavelength, $r_e$ the classical electron radius, $C$ the polarization factor, $\gamma$ 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 $\gamma$ are equal to 1.

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

$$\omega_{D,40} = \omega_{D,Cu} \frac{\lambda_{40}^2 \sin 2\theta_{B,Cu}}{\lambda_{Cu}^2 \sin 2\theta_{B,40}} = 6.6 \cdot 10^{-6} \text{rad}$$  \hspace{1cm} (2)

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

Considering the intrinsic resolution of the crystal a constant $\Delta E$ 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.

$$R_T = 1 \cdot \left( \frac{\Delta E}{E} \right)_{intr} \cdot 10^3$$  \hspace{1cm} (3)
According to Table 1 in the work of Sanchez del Rio and Mathon\textsuperscript{1} even at $\psi = 5\omega_D$

the value for $R_T$ changes by less than 2%.

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

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

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

References
