

Test of an electrochemical cell body for studies of solution (radio)chemistry at ambient and elevated temperature ($\leq 120^\circ\text{C}$)

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Background and Aims of the experiment

The study of electrochemical reactions by X-ray absorption spectroscopy can provide unique information on the thermodynamic and kinetics properties of systems in (radio)chemistry [1-4], catalysis [5], environmental geosciences [6-8], and materials [9]. However studies using *ex situ* preparation of the sample are generally limited by their poor ability to reveal transient electroactive species. Also, the electrochemical properties of some systems of interest may be affected by sample transport and beam exposition, and the absence of an *in situ* control of the electrochemical properties complicates data interpretation. Of critical importance are preparations at low redox conditions, which are easily oxidized by air, and high-temperature products which may be altered during sample transport.

To avoid these caveats related to *ex situ* preparation of the sample, an electrochemical device for *in situ*, real-time study of (radio)chemical reactions in solutions and suspensions by synchrotron radiation on the MARS beamline at SOLEIL has been developed jointly by the CEA and CNRS (Subatech) [10]. Because this device is to serve the need of a large community, rather than a single research team, it is developed along several specifications aiming at increasing its versatility. The purpose of our experiment was to assess some of these requirements, namely:

- the possibility of recording spectra in fluorescence and transmission modes,
- the possibility of working from ambient to elevated temperatures of 90°C , possibly 120°C ,
- the possibility of using the cell on conventional beamlines, meaning that the cell is to be contained in confinement barriers.

Outcome of the experiment

Several cell configurations were tested on the FAME beamline using a beam of $300 \times 200 \mu\text{m}$ (hvx) footprint. First, we evaluated the quality of the windows which were milled in the cell body for X-ray absorption spectroscopy measurements. To this end, we collected EXAFS and XANES spectra on the cell filled with 0.1 mol L^{-1} (M) Na_2SeO_3 or 10^{-3} M Na_2SeO solutions in transmission and fluorescence detection modes, respectively. Figure 1 shows that high-quality data could be obtained, in fluorescence, and especially in transmission mode. Only one monotonic oscillation

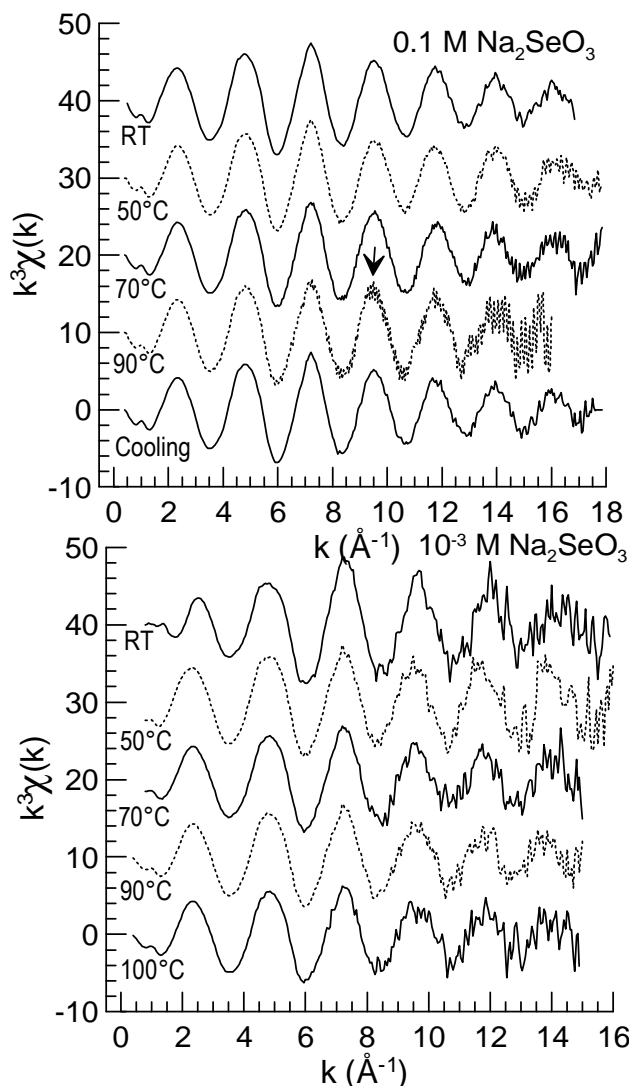


Figure 1. EXAFS spectra for 0.1 M (top) and 10^{-3} M (bottom) Na_2SeO_3 solution in the electrochemical cell at various temperatures.

corresponding to oxygens binding selenium is observed, and little if any noise of spectral disruption is observed over the whole k-range, especially in transmission mode. These preliminary data opened the door to further evaluation of the cell integrity and performance at high temperature.

To perform the second test, a temperature sensor plunging into the solution was glued onto the cell lid, and the cell body was fitted with heating bands and positioned within the second confining barrier. The cell temperature was increased sequentially, and maintained at constant temperatures by using a retroactive thermostatic loop. Between two and three X-ray absorption spectra were collected in transmission mode at 50, 70, and 90°C for 0.1 M Na₂SeO₃, and in fluorescence mode at 50, 70, 90 and 100°C for 10⁻³ M Na₂SeO₃. Clearly, in fluorescence mode the increase in temperature did not affect the collected spectra in a systematic way, demonstrating the robustness of the cell setup (Figure 1). In transmission mode, small-period, saw-like oscillations were observed on EXAFS oscillations at high k (figure 1, arrow). These oscillations were attributed to small variations in the optical path due to periodic re-heating of the cell. This interpretation was confirmed by recording a last transmission spectrum on the cell during free cell cooling: the saw-like oscillations were not observed.

Future expectations

This successful collection of high-quality EXAFS spectra at high temperatures paves the way for future developments. First, the cell has been tested up to 100°C only due to technical limitations on the heating regulator. However, flawless operation at this temperatures, and resistance test demonstrating that the cell holds its integrity up to 150° both suggest that hydrothermal conditions (up to 150°C) will be easily attained and maintained over a period of hours, possibly days. Second, electrochemical experiments under synchrotron radiation may now be performed, knowing that the changes in x-ray absorption spectra directly relate to changes in elemental speciation. Thus, the electrochemical setup will be used to probe oxydo-reductions reactions of trace elements of radiochemical interest, such as selenite. These experiments will permit to evaluate the capacity of the electrochemical setup to perform *in-situ* oxydo-reduction reactions for which transient chemical species are suspected. Next, the cell will be used to study solution speciation of cerium, a surrogate for plutonium, as a function of solution composition, temperature, pH and Eh conditions. The experience accumulated during these studies will be desirable to perform *in situ* studies of oxydo-reduction reactions of radioelements of interest, such as technetium and plutonium, with a maximal level of security. Eventually, reactions of complexation and *in situ* titrations will also be allowed by adding inlets to the cell body, thus increasing the versatility of this electrochemical setup.

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