A portable powder-liquid high corrosion-resistant reaction cell for in situ X-ray diffraction and absorption studies of heterogeneous powder-liquid reactions and phase transformations

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Abstract. A portable powder-liquid high corrosion-resistant reaction cell has been designed to follow in situ reactions by X-ray powder diffraction and X-ray absorption spectroscopy techniques in transmission mode. The cell has been conceived to be mounted on the experimental stations for diffraction and absorption of the Spanish CRG SpLine-BM25 beamline at the ESRF. In the case of the diffraction technique, data can be collected with either a point detector or a two-dimensional CCD detector. Using the 2D-CCD camera, the cell can be used for time-resolved in situ studies of phase transitions and reactions. Powder reactants and/or products are kept at a fixed position in a vertical geometry in the X-ray pathway, which is minimized in order to reduce the X-ray absorption by the reaction bath. Sample is fixed by a porous membrane under forced liquid reflux circulation, assuring total powder-liquid contact, with an accurate temperature control in the range from 20 to 220ºC.

1. Introduction
The use of adequate techniques and experimental set-ups capable of producing detailed information during heterogeneous reaction process is one of the most important goals for chemistry research. X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (XAS) are two techniques that are very well placed to fulfill these requirements. Both techniques are also powerful tools for electronic and crystallographic structure analysis, for time-resolved in situ studies of phase transitions and pathway reactions. However, even for these two well-suitable techniques, a special challenge is the case of powder-liquid reactions, as many reactions require the presence of a dissolvent to make possible or catalyze the solid phase transformation. Generally permanently shaking of the reactants is required in order to guarantee the reaction take-place.

Several variety of cells have been developed to solve the needs that the heterogeneous reaction measurements require\textsuperscript{1-6}. The main innovations for the cell presented in this work are: the fact that it can handle solid–liquid heterogeneous reactions keeping the powder reactants and/or products in the beam pathway in a fixed position during the chemical reaction, assuring total powder-liquid contact, accurate temperature control and perfect compatibly with XRD and XAS experiments.

The cell has been designed to be mounted at the XAS station and the six-circle multipurpose diffractometer of SpLine, the Spanish CRG BM25 beamline at the ESRF. In the latter case, the set-up
takes advantage of the 2D-CCD (Photonic Science) detector on the diffractometer. The cell performance has been demonstrated by following the crystallization process in aqueous solution of the cooper-isoleucine amino acid complex by XRD and XAS. In this work, the phase transformation of copper carbonate and the amino acid in boiling aqueous solution has been in situ studied and the complete reaction pathway of the Cu(Isoleucine)$_2$ complex has been obtained to correlate the reaction pathway with the initial and final atomic structure.

2. Solid-liquid reaction cell set-up

The six circle diffractometer has its main axis in the vertical and is able to house loads up to 50 kg with a free space of 800 x 800 mm$^2$, so the portable solid-liquid cell can be easily accommodated. It is coupled with a point and a 2D-CCD detector (250x125 mm$^2$ active area). The combination of them makes possible the study of in situ time resolved, preferred orientations small and wide angle XRD experiments. The 2D-CCD detector is mounted on a motorized stage with 4 degrees of freedom (three translations $x$, $y$, $z$ and a tilt $\theta$) and it can be rotated and placed with the larger side either vertically or horizontally, in order to maximize the accepted solid angle along or perpendicular to the synchrotron polarization plane. The use of a beam stopper is required. The camera produces 250x125 mm, 33 megapixel resolution images with 32.8 microns pixel size, with a final resolution of 7651x3825 pixels. A typical full powder diffractogram can be recorded in a minimal time of 200 ms, which defines the minimal kinetic timescale. The d-space resolution can be adapted to the experimental requirements, changing either the detector-cell distance or the photon beam wavelength.

For XAS station, the data are also taken in transmission mode and no space problems are found. The stability and the precise performance of the cell are essential for the XAS and XRD experiments. The novel cell has been designed taking into account that: (i) the powder must be kept in the X-ray impact position during the reaction process, and (ii) it has to be a short X-ray path, as the measurements are done in transmission mode.

The main body is finished of Teflon material to avoid reactants corrosion, being the temperature range from room temperature (RT) up to 200 degrees; however, it can be built on different materials to vary the capabilities of the cell. The body is covered by a stainless steel protection. The cell is formed of three main parts (Figure 1): the body which contains the liquid channel (with the corresponding openings for distillation column, thermometer and powder holder), the powder holder and the protection/furnace cover.

In Figure 1, a scheme of the cell is shown. In the interior cavity, there is the channel where the liquid flows along the main body. The solution goes through it under reflux conditions, forcing the liquid circulation. The solvent channel is connected with the exterior through seven exits: three in the upper, two in the central and two in the lateral positions. At the top, there are three main holes; two in conical form (14/23), which are foreseen to locate a control thermometer or a liquid reservoir (left) and a distillation column (right) to guarantee the reflux conditions, and one elongated central aperture of 21x3 mm$^2$ (length and width) and 32 mm depth which is used to position the powder holder. The incorporation of the liquid solvents is made through one of the conical apertures of the top side. In the middle of the long side of the cell body, a 12 mm cylindrical aperture is used for the incident X-ray beam. At each of the cell long sides an additional 20 mm outlet disk is placed to allocate a metal window support. And at the short sides, two extra holes are made for construction reasons and they are used to facilitate the cell cleaning after each experiment. In the two conical holes at the body, there are allocated a thermometer and a reflux system; however other devices can be mounted on them depending on the reaction requirements. Besides, there are additional channels in the cell that are not in direct contact with the liquid canal, four of them are used to locate cartridge heaters to heat the solution by thermal conductivity, providing a good temperature control.

The powder holder is located in the middle of the cell body; the cell dimension is 4.5 mm through the X-ray direction. The reduced cell dimension in this region and consequently the X-ray pathway allows the measurements in transmission mode. Two Kapton/Teflon windows of 5 mm aperture diameter are foreseen for the in-coming and out-going X-ray beam. The out-going solid angle
aperture has been chosen to maximize the diffracted angular acceptance, covering a maximal angular range of ±45°. The chosen angular acceptance allows a maximal d-space resolution of 0.3 Å for a wavelength of 0.6 Å. The sample holder has a pocket shape opening where the powder is placed and kept at a fixed position. The powder is covered by a porous membrane envelope with a porous size lower than the grain size of the powder, but high enough to assure the liquid circulation. For the test measurements presented in this work, a porous Teflon membrane with a porous size of about 12.5 microns (Goodfellow FP301020) has been used, which allows the passage of the liquid through the solid sample and traps the powder in the cavity. The powder holder presents three side holes of 2 mm diameter along the main channel direction in order to facilitate the liquid circulation through the powder. Different membrane’s porous dimensions can be used depending on the grain size; and powder from 500 nm to 50 µm grain size can be studied with an optimum contact with the flow solution (membrane available, for example, from Goodfellow).

The stainless steel protection covers the Teflon body offering physical resistance. Once the entire cell is mounted, a special stainless steel box-plate avoids the possibility that the solvent sheds onto the station’s tower. By means five independents degree of movements the cell can be moved into the X-ray beam in a very precise and reproducible way.

![Diagram of the solid-liquid reaction cell](image)

Figure 1. a) General scheme of the solid-liquid reaction cell and b) real image on the diffractometer.

3. X-ray measurements: Cu-Isoleucine crystallization

The crystallization reaction was carried out with 0.4 mmol of CuCO₃ (fluka) and 0.8 mmol L-Isoleucine (fluka) (10% excess) in boiling aqueous solution and it was followed by XRD and XAS techniques. The reaction temperature was varied from RT to 100°C for Cu(Ile)₂ formation.

Diffraction experiments have been carried out at 14.89 keV with a beam spot size of 500 µm × 500 µm. The complete reaction pathway has been followed using the 2D detector. Resulting images were integrated with XOP2.3 program⁷. The CCD detector was mounted off-center to record the weak Debye-Scherrer diffraction rings, reaching up to 0.54 Å of d-space resolution at the edge of the detector and a 2x2 binning was used. Data were taken at 30 seconds of exposure time to obtain a better signal-to-noise ratio, with a distance sample-detector of 197 mm (20 maximum ~ 50°). On the other hand, XAS measurements have been performed at the Cu k-edge using two identical gas-filled ionization chambers. XAS measurements were analyzed with ATHENA software⁸.

Once the solid mixture is allocated in the sample holder, the cell is filled with water at RT. The role of the water is to dissolve the initial reactants, and also to enhance the mobility of the ions. The reaction is monitored through CuCO₃ concentration decreases while the Cu(Ile)₂ concentration increases. The chemical reaction was carried out and the formation of Cu(Ile)₂ was followed as a function time. The reaction is exothermic and the dissolved isoleucine and Cu ions react, obtaining the complex formation (Figure 2a). The diffraction study shows an immediate reaction between initial products, as Cu(Ile)₂ complex is observed on the first diffractogram collected (see peak at 2θ ~ 4.3°). As the mobility of the reactants is difficult because of the presence of the porous membrane, the volume at the powder holder is over saturated with the reaction products, producing their precipitation that remains in the same sample holder position instead of flowing across the cell. This configuration allows the following of the chemical reaction, and its evolution as a function of time and temperature.
is showed on Figure 2a. After 130 minutes under reflux, the initial reactant L-Isoleucine is still
detected on the pattern, which coincides with the excess of product added while all the CuCO₃ reacted
to achieve Cu(Ile)₂. On the CCD images (not shown here), the observed Debye-Scherrer rings are
continuous and uniform, indicating a lack of preferential orientation, as it is expected.
Cu k-edge XAS spectra of the evolution from the initial reactants to the final product are
showed in Figure 2b. Two different features can be distinguished in the spectra evolution: a single
peak at the beginning of the reaction, whereas an extra peak can be distinguished at the end of the
reaction, with a decrease on the intensity around 9060eV (Figure 2b). After the reaction, the obtained
data agreed with the expected spectra of Cu(Ile)₂ complex. In this particular reaction, the separation
of the different Cu species is difficult, since the oxidation state of Cu ions does not change appreciably
between the different compounds (reactant and products). So, the XAS signal is an average of present
species. As occurs in the XRD patterns, the observed changes in the spectra from the beginning
demonstrated that the reaction take place immediately when water come in contact with the products.

![Figure 2. Crystallization process of the Cu(Ile)₂ complex by a) XRD and b) XAS. (*:Cu(Ile)₂ complex)](image)

**4. Conclusions**
A novel reaction cell has been designed to follow *in situ* powder-liquid reactions. Powder is
mounted and placed at the X-ray beam position inside a high corrosion resistance cell (Teflon
material). The powder is kept in the beam position with a porous membrane, while the liquid circulates
across its channels, assuring a total contact with the sample. The X-ray pathway has been reduced to
perform the measurements in transmission mode. The temperature of the liquid is controlled, covering
the range for a cell built in Teflon material from RT up to 220 °C.

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**References**
[1] Villain F et al 1993 *Anal. Chem.* **65** 2545
[2] Norby P et Hanson J C 1998 *Catal. Today* **39** 301
[3] Alison H et al 2003 *Phys. Chem. Chem. Phys.* **5** 4998
[4] Grunwaldt J D et al 2005 *Rev. Sci. Instrum.* **76** 054104
[5] FitzGerald V et al 2007 *J. Synchrotron Rad.* **14** 492
[6] Wall J et al 2011 J. Appl. Cryst. **44**, 429
[7] Sanchez del Rio M *Synchrotron Data Analysis Using XOP*, in Synchrotron Radiation in
Mineralogy, [http://www.ehu.es/sem/revista/seminarios_m.htm#Vol6](http://www.ehu.es/sem/revista/seminarios_m.htm#Vol6).
[8] Ravel B and Newville M 2005 *J. Synchrotron Rad.* **12** 537