ESRF	**Experiment title:** In situ XAS studies of Pt-Ni electrode/ionic liquid interface for electrosynthesis application	**Experiment number**: CH6530
Beamline: ID26	**Date of experiment**: from: 22.11.22 to: 29.11.22	**Date of report**: 20/02/2023
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Report:

During experiments at ID26 we have investigated the role of ionic liquid, IL (EMIM OTf), into the stabilization of Ni- and PtNi-based electrocatalysts *in situ* in acidic (0.1 M $HClO_4$) and alkaline (0.05 M NaOH) environments. Specifically, we collected Ni Kα HERFD XANES and EXAFS spectra under potential (potentiostatic protocol)/current hold (galvanostatic protocol) in a three-electrode spectroelectrochemical cell (**Figure 1**). Ni- and PtNi-based electrodes (thickness ca 30 nm) were manufactured by electron-beam physical vapour deposition on a carbon paper (Toray Carbon Paper, TGP-H-60) substrate at Max-Planck-Institut für Eisenforschung (MPIE, Germany). In total 27 protocols have been tested with and without IL. The spectra were analyzed using python-based scripts developed at ID26 beamline.

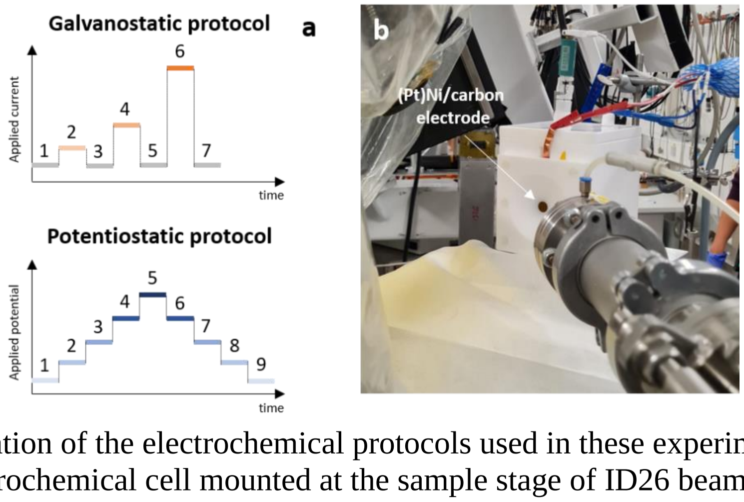

Figure 1. a. Visualization of the electrochemical protocols used in these experiments. **B.** Photo of the electrochemical cell mounted at the sample stage of ID26 beamline.

Figure 2a and **b** show Ni K edge XANES spectra recorded on PtNi-based electrode in acidic electrolyte without and with IL presence, respectively. Please note that not all the potentials are shown in the panels for the sake of clarity. We observe that in the absence of IL an increase of the applied potential leads to gradual changes in the intensity of the white line and of the pre-edge that can be correlated with a partial oxidation of Ni sites. Interestingly, these changes are not reversible when we decrease the potential back, moreover, the oxidation process continues (**Figure 2a**). In case of IL-containing electrolyte, increase of the applied potential also leads to partial oxidation of Ni sites, however in this case, this process is reversible (**Figure 2b**). Further oxidation of

Ni may lead to its leaching from the electrode, which is currently being investigated by dissolution studies using a scanning flow cell (SFC) connected to the inductively coupled plasma mass spectrometer (ICP-MS). The tests are performed on the same group of samples following the experimental protocols used during this beamtime and cover besides Ni dissolution also the dissolution of Pt in the PtNi alloys. At least four XANES spectra (30sec each) were collected at each potential (or current in case of galvanostatic protocol), allowing the time-resolved analysis of Ni K edge data. **Figure 2c** and **d** show a sequence of Ni K edge spectra collected at 1.5V vs RHE (reversible hydrogen electrode) in the absence of IL and with the latter, correspondingly (the averaged spectra are shown in panels **a** and **b**, respectively). The comparison of these data demonstrates the difference in Ni sites surface behaviour under applied potential depending on the presence of IL.

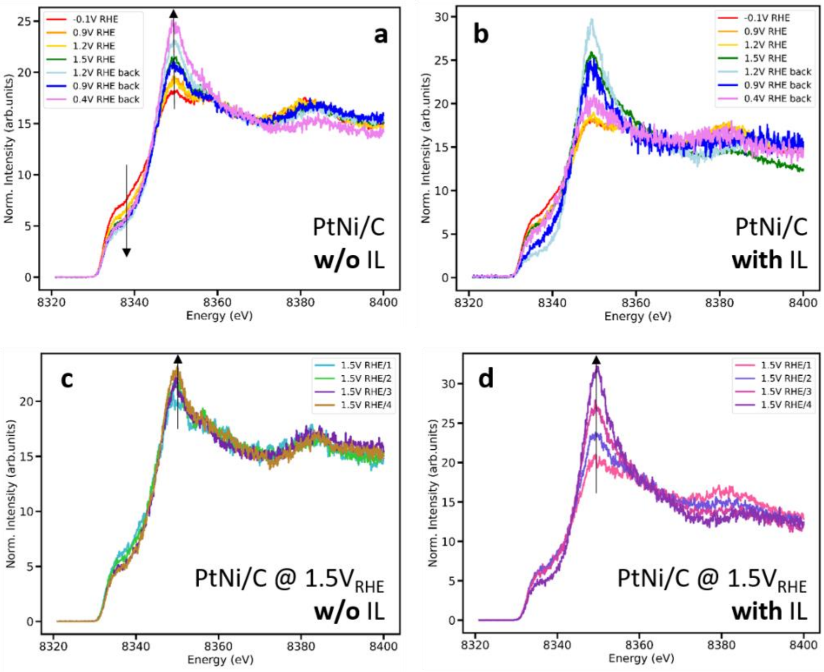

Figure 2. Ni Kα XANES spectra recorded on PtNi-based electrodes in acid electrolyte with and without IL during potentiostatic protocol.

Figure 3 compares Ni K edge spectra collected at 0.3 mA·cm^2 at different stages of galvanostatic protocol (**Figure 1a**) in alkaline electrolyte with and without IL. While Ni sites remain almost unchanged during this protocol (**Figure 3a**), the addition of IL into the electrolyte does modify Ni surface. Specifically, we observe a shift of Ni white line towards higher energies after applying high current values (stage 5 and 7 of the protocol). We also recorded EXAFS spectra under the same experimental conditions in order to investigate the changes in local structure of Ni sites. These data are still under analysis.

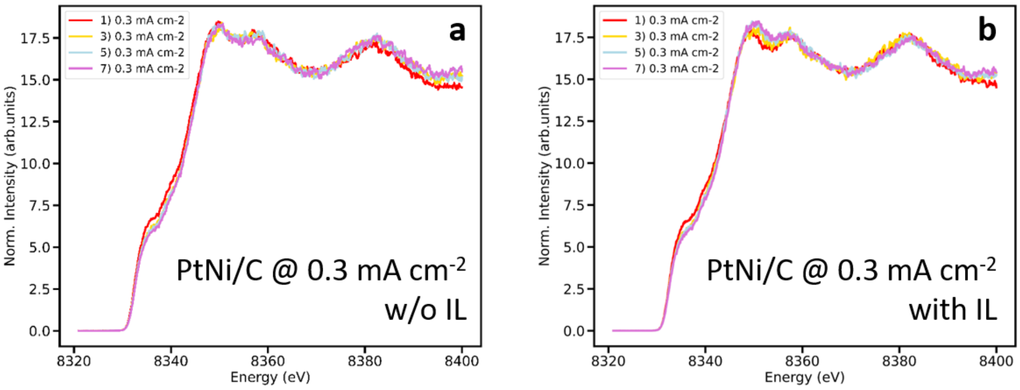

Figure 3. Ni Kα XANES spectra recorded on PtNi-based electrodes in alkaline electrolyte with and without IL during galvanostatic protocol.

Except for *in situ* data, we also collected *ex situ* spectra on the reference materials, pristine and post-mortem catalysts. As it was mentioned above, the XAS data will be supplemented by *in situ* dissolution results as well as post-mortem characterisation of the materials studied here using X-ray photoelectron spectroscopy. The publication(s) featuring these results will be prepared asap.