

## Report proposal 26-01-1014 DUBBLE 19<sup>th</sup>- 22<sup>nd</sup> February 2015

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**Background.** An effective protective coating for Pb was found in the use of coatings deposited from solutions of saturated linear monocarboxylates of the type  $\text{CH}_3(\text{CH}_2)_{n-2}\text{COONa}$  ( $\text{NaC}_n$ ). Protection is due to the growth of a crystalline metal monocarboxylate layer which passivates the surfaces. Higher chain length and higher concentrations will result in higher effectiveness. However, the solubility of these compounds drastically decreases with increasing chain length, and C chains longer than  $\text{C}_{12}$  have hardly been investigated. We have developed the idea of reacting the lead samples with the pure melted acids, and in this beamtime we have studied the formation of coatings following this procedure.

Our group has developed an environmental cell (eCell) which can be used for a particular chemical treatment (for example immersion of the sample in a solution), while the metal surface is analysed through a thin electrolyte layer using a spectroscopic technique. eCell allows for time-resolved *in-situ* monitoring of coating formation using synchrotron X-rays. The cell is a cylinder containing a piston which is driven along the bore by a stepper motor. The sample is mounted on the piston, allowing the sample to be moved from a fully "immersed" position to a "diffraction" position which is 125  $\mu\text{m}$  from the window.

**Experiments.** Experiments were carried out at BM01A through the agreement between DUBBLE and the Swiss Norwegian Beam Line. We travelled on the 16<sup>th</sup> February, and on 17<sup>th</sup> and 18<sup>th</sup> February we setup our experiment on the beamline (preparation of the cell, interphasing of our electronics to the beamline software and hardware, alignment of the sample, etc.).

We followed in real time the growth of 3 different lead-carboxylate compounds:  $\text{Pb}(\text{C}_7)_2$ ,  $\text{Pb}(\text{C}_{12})_2$  and  $\text{Pb}(\text{C}_{14})_2$ . The last two compounds show the best anticorrosion performance when studied by other techniques in the lab, and in addition the pure acids show relatively low melting points (46° and 54° respectively).  $\text{Pb}(\text{C}_7)_2$  makes an interesting comparison since  $\text{C}_7$  is already a liquid at room temperature, and hence won't co-crystallize together with our compounds of interest during the coating formation.

For each departing compound ( $\text{C}_7$ ,  $\text{C}_{12}$  and  $\text{C}_{14}$ ), 4 different types of experiments where performed:

1-A bare lead coupon was immersed in the  $\text{C}_n$  solution, and the electrode was moved towards the X-ray diffraction position in the cell at regular intervals every 10 minutes.

2-Different lead coupons were immersed in the  $\text{C}_n$  solution, and the electrode was moved towards the X-ray diffraction position in the cell at increasing time intervals: 20 mins, 40 mins, 1 hour, 2 hours, etc.

3-X-ray diffraction patterns where measured at regular intervals every 15 seconds in real time, as the electrode dried out just after been taken out of the  $\text{C}_n$  solution.

4-X-ray diffraction patterns where measured at regular intervals as a freshly formed coating was rinsed in ethanol (the pure acid is soluble in ethanol, whereas the lead carboxylate is not).

**Preliminary results and conclusions.** While a detailed analyses of the data is still to be carried out, we can advance the following partial results/conclusions. Well-defined diffraction patterns, corresponding to crystalline compounds are only observed after the electrode has been out of the solution for at least 2 minutes. This was puzzling, since every time we had previously analysed this compounds in a laboratory diffractometer (however, many hours after the layer had been formed) we observed a well-defined crystalline pattern. While mass gain experiments in the lab had shown that the layers continuously grow in time for at least 50 hours during continuous immersion. Synchrotron experiments showed that there's continuous growth for about 3 hours, and afterwards, the crystalline compounds are no longer visible. This data needs further analysis. Possible hypothesis include the formation of an amorphous layer, that eventually recrystallizes with time, the partial destruction of thick layers due to convection. We need to analyse our data in detail (including the evolution of the background in the different time-lapse XRD images).

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