EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Studies of solid electrolyte interfaces and SEI	**Experiment number**: MA2268
Beamline: BM32	**Date of experiment**: from: 12th December to: 16th December	**Date of report**: 25/02
Shifts: 9	**Local contact(s)**: RIEUTORD	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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*Danet Julien
*Boniface Maxime

Report:

We performed high energy reflectivity experiment at the silicon/ electroilyte interface.
The electrolyte was the standard EC/DEC/LiPF6 electrolyte, the positive electrode was Lithium Metal and the negative electrode was monocrystalline silicon, heavily doped so as to be conductive. The contact was made through stainless steel electrode on which Lithium and Silicon were contacted. Separation of the two electrodes was made by a PEEK cell body, cylindrical in which the window for X-rays was directly machined.

We ramped the potential from the 3V open circuit voltage down to 0 V and back using a voltameter cycler, at a rate of 0.1mV/s. Flowing current was measured throughout the experiment. Reflectivity curves were taken in loop, including periodic re-alignment scans (angle and height) and grazing-incidence diffraction scans. Typically 400 reflectivity scans were taken throughout the cycle loop.

The energy was chosen to 27keV ensuring a good transparency of the 15mm diameter cell. Beam size was typically 50µm high.

A series of reflectivity curves is shown below as a function of decreasing potential voltage.

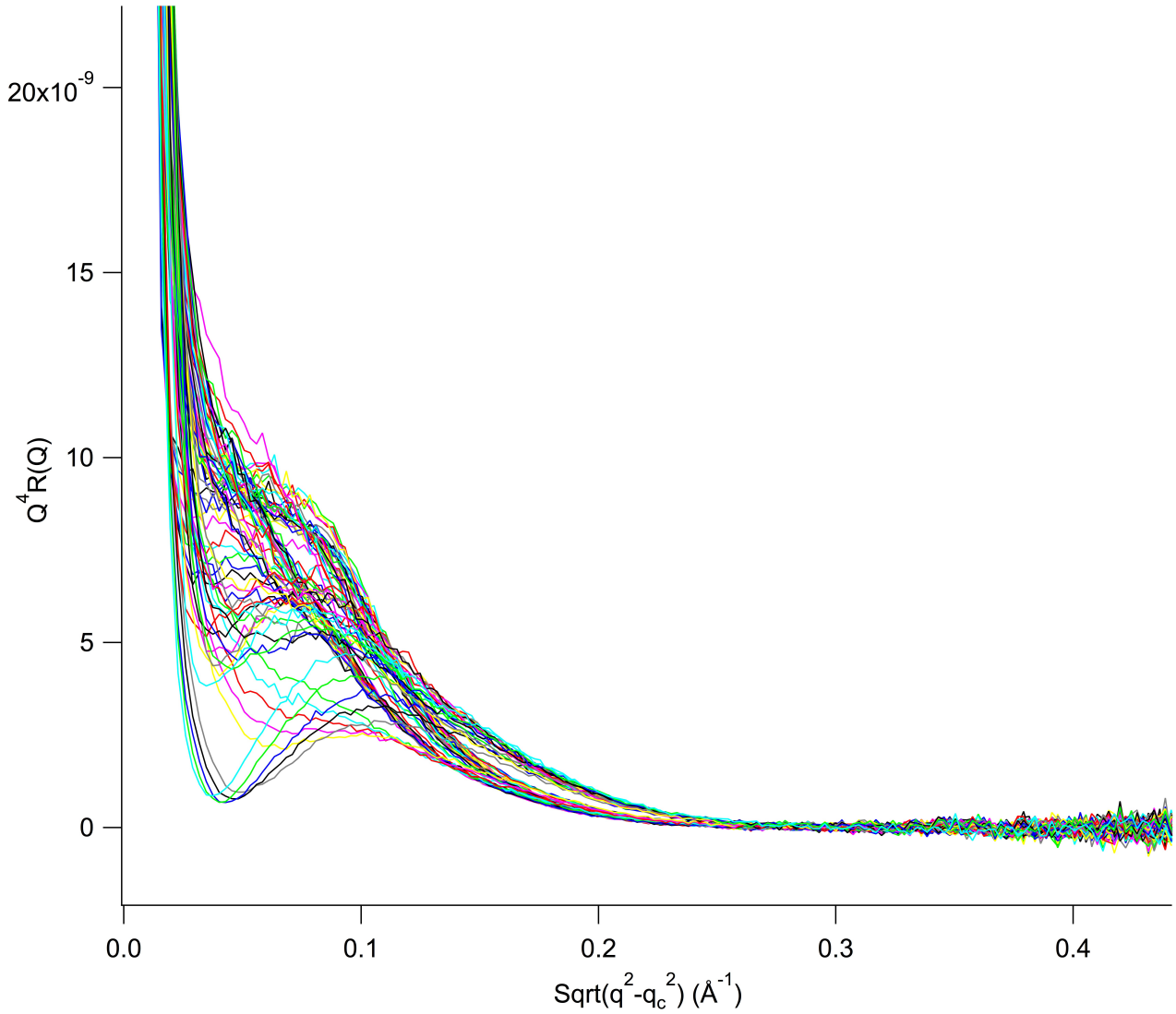

Fig1. Series of relection curves from 3V to 0V. A clear evolution of the interface reflectivity is visible upon potential change

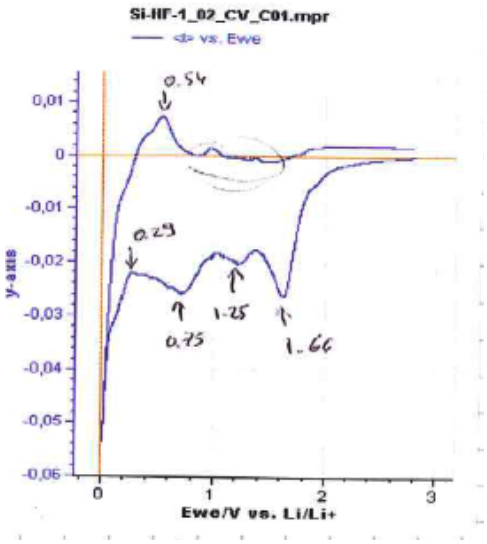

Fig.2 Voltamogram obtained during the experiment showing the occurrence of electrochemeical at different potentials. These evolutions can be matched with reflectivity change, both being associated to interface layer buildup or interface change.

The reflectivity curves can be fitted to models using the standard algorithms. For the sake of simplicity we used kinematical approximations to fit the data, the full dynamical treatment being unecessary for q>>qc data. Note that to extend the range of validity of kinematical treatment, we used refraction corrected values for q (q'=sqrt(q^2-qc^2)). Once a profile is found using kinematical approximation fits, the solution is validated by a full calculation including critical angle using standard optical matrix formalism.

Electron density profiles can be extracted from the data with a sequence of layer formation that seems to be more complex than expected.

The first evolution corresponds to the formation of a thick diffuse layer with reduced electron density compared to the electrolyte. The presence of this reduced density layer against the electrode is signed by an increase of I(q=0). A fit to the data gives a thickness in the 7nm range with a density reduced by typically 10% of the Si/electrolyte density difference. This evolution seems to start already at a voltage of 1.66V where a peak in the electrical current occurs.

In a second stage the density at the interface seems to increase again, with a reduction of the q=0 intensity. The diffuse character of the layer seems to be maintained.

In a third stage a very well defined layer appears at low potential, with a density smaller than the electrolyte or the diffuse layer. Its interfaces and thickness (t=1.8nm) are well defined and below the diffuse layer thickness (estimated to 6 to 7nm with a 3nm transition zone between this layer and the electrolyte).

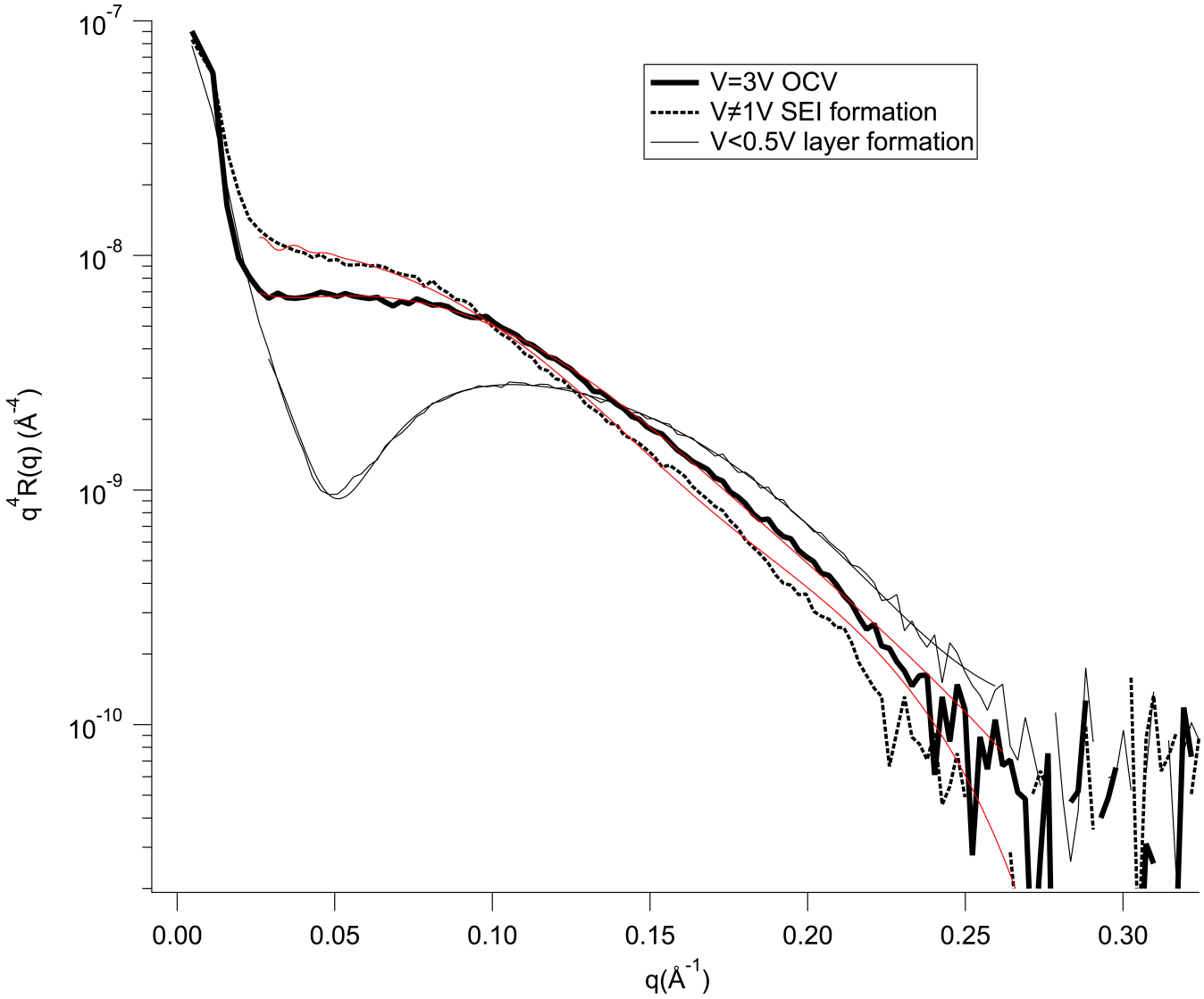

Fig3. 3 typical curves extracted form Fig1 series. The evolution of reflectivities are clearly visible.