ESRF	**Experiment title: Real-time Studies of Metal Electrodeposition: Temperature Effects in Electrochemistry**		**Experiment number**: 28-01-709
Beamline: BM28	**Date of experiment**: from: 11/5/05	to: 27/05/05	**Date of report**: 1/4/2007
Shifts: 17	Local contact(s): **Laurence Bouchenoire**		*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Chris Lucas*, Ben Fowler*, Mark Gallagher*, David Mercer* (University of Liverpool)

Paul Thompson* (XMaS)

Report:

This experiment continued our studies of the effects of temperature on the atomic structure and reactions at the electrochemical interface. The results have been incorporated in an article that has been submitted as a letter to Nature. The abstract is attached below:

Temperature-induced changes in the atomic structure at the charged solid-liquid interface

Christopher A. Lucas[1], Paul Thompson[1], Ben Fowler[1], David Mercer[1], Michael Cormack[1], Vojislav Stamenkovic[2], Dusan Strncnik[2], Andreas Menzel[3], Vladimir Komanicky[2], Kee-Chul Chang[2], Hoydoo You[2] and Nenad M. Marković[2]

[1]*Oliver Lodge Laboratory, Department of Physics, University of Liverpool, Liverpool, L69 7ZE, United Kingdom*

[2]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*

[3]*Swiss Light Source, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*

The study of charge transfer across electrochemical interfaces has been an enduring theme in a wide range of science and is of importance to clean energy production and storage[1-4], photochemical energy conversion[1,2], corrosion[5] and the functioning of biological membranes[6,7]. At electrified solid-liquid interfaces phenomena, such as surface restructuring and the adsorption of reactive and spectator species, give rise to a rich diversity of tunable ordered structures which determine both the reactivity and stability[8,9]. The application of *in-situ* structural probes with atomic-scale resolution has allowed the electrochemical response to be directly correlated with the interfacial atomic structure and enabled structure-function relationships to be established[10]. All such experiments, however, have been performed at ambient temperature and the effect of temperature changes on the potential-driven phase transitions at the electrochemical interface has yet to be considered in any systematic way. In this letter it is illustrated that small temperature changes can have a dramatic effect on the interface structure. By focusing on two canonical systems, the surface reconstruction of Au[11-13] and the molecular adsorbate structures of CO on Pt[14,15], it is demonstrated that, in addition to the electrode potential, the temperature plays an *equally* important role in determining the interface structure. The results have widespread implications for future research in both fundamental and applied electrochemistry as combined temperature/potential effects may be exploited to control charge transfer processes.

1. Nature Insight. Materials for clean energy. *Nature* **414**, 331-377 (2001).
2. Sustainability and Energy. *Science* **315**, 733-870 (2007).
3. Stamenković, V. R. , Fowler, B., Mun, B. S., Wang, G., Ross, P. N., Lucas, C. A. & Marković, N. M. Improved Oxygen Reduction Activity on $Pt_3Ni(111)$ via Increased Surface Site Availability. *Science* **315**, 493-497 (2007).
4. Stamenković, V. R. , Mun, B. S., Arenz, M., Mayrhofer, K. J. J, Ross, P. N., Lucas, C. A. & Marković, N. M., Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces. *Nature Materials* **6**, 241-247 (2007).
5. Renner, F. U., Stierle, A., Dosch, H., Kolb, D. M., Lee, T. –L. & Zegenhagen, J. Initial corrosion observed on the atomic scale. *Nature* **439**, 707-710 (2006).
6. Hynes, J. T., Physical chemistry: The peripatetic proton. *Nature* **446**, 270-273 (2007).
7. Sanguinetti, M. C. & Tristani-Firouzi, M. hERG potassium channels and cardiac arrhythmia. *Nature* **440**, Insight (2006).
8. Markovic, N. M. & Ross, P. N. Surface science studies of model fuel cell catalysts. *Surf. Sci. Rep*. **45**, 117-230 (2002).
9. Magnussen, O. M. Ordered anion adlayers on metal electrode surfaces. *Chem. Rev*. **102**, 679-726 (2002).
10. *Interfacial Electrochemistry*, edited by Wieckowski, A. (Marcel Dekker Inc., 1999).
11. Kolb, D. M., Reconstruction phenomena at metal-electrolyte interfaces. *Prog. in Surf. Sci.* **51**, 109-173 (1996).
12. Ocko, B. M., Wang, J., Davenport, A. & Isaacs, H. S. In-situ x-ray reflectivity and diffraction studies of the Au(001) reconstruction in an electrochemical cell. *Phys. Rev. Lett*. **65**, 1466-1469 (1990).
13. Gao, X. & Weaver, M. J. Electrode potential-induced reconstruction of Au(100): Effect of chemisorption on nanoscale dynamics as probed by in-situ scanning tunnelling microscopy. *J. Phys. Chem.* **97**, 8685-8689 (1993).
14. Villegas, I. & Weaver, M. J. Carbon monoxide structures on platinum (111) electrodes: A synergy between in-situ scanning tunneling microscopy and infrared spectroscopy. *J. Chem. Phys.* **101**, 1648-1660 (1994).
15. Lucas, C. A., Marković, N. M. & Ross, P. N. The Adsorption and Oxidation of Carbon Monoxide at the Pt(111)/electrolyte Interface: Atomic Structure and Surface Relaxation. *Surface Science* **425**, L381-L386 (1999).