

***In situ* Stress and Nanogravimetric Measurements during De-alloying of PtCu Thin-film Electrode**

**V.A. Sethuraman,¹ D. Vairavapandian,¹
M.C. Lafouressee,² N. Karan,¹ S. Sun,³ U. Bertocci,²
G.R. Stafford,² P.R. Guduru¹**

¹School of Engineering, Brown University
182 Hope St., Providence, Rhode Island 02912, USA

²National Institute of Standards and Technology,
Materials Science and Engineering Laboratory, 100
Bureau Drive, Gaithersburg, Maryland 20899, USA

³Department of Chemistry, Brown University
324 Brook St., Providence, Rhode Island 02912, USA

Enhanced catalytic activity of de-alloyed PtCu electrodes towards oxygen reduction reaction had been demonstrated in thin-film and core-shell geometries.¹⁻⁵ The enhancement in catalytic activity is typically attributed to strained Pt layer (in thin-film electrodes) and Pt shell (in core-shell electrodes). The magnitude and the nature (compressive/tensile) of the strain on de-alloyed Pt were estimated thus far using lattice-constant measurements (*via* X-ray diffraction) on de-alloyed electrodes. In this work, we report real-time stress and nano-gravimetric measurements made during de-alloying of thin-film PtCu electrodes. *In situ* stress measurements were made using cantilever-deflection method, and gravimetric measurements were made using an electrochemical quartz crystal nanobalance.

Upon de-alloying *via* successive voltammetric sweeps between 0.05 V and 1.15 V vs. SHE, compressive stresses develop in thin-film PtCu electrodes. *In situ* and *ex situ* gravimetric measurements indicate 0.5% (by wt.) of Cu removal from PtCu electrode; this corresponds to 1 nm or less of a Pt-enriched surface on the PtCu electrode. These measurements indicate a Pt enriched surface under a compressive stress of 1.5-2GPa.

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References

1. Koh and Strasser, *J. Am. Chem. Soc.*, **129**, 12624-12625 (2007)
2. Liu *et. al.*, *J. Electrochem. Soc.*, **154**, B1192-B1199 (2007)
3. Mani *et. al.*, *J. Phys. Chem. C*, **112**, 2770-2778 (2008)
4. Strasser *et. al.*, *Nat. Chem.*, **2**, 454-460 (2010)
5. Toney *et. al.*, *Chem. Mater.*, **22**, 4712-4720 (2010)