Electronic Supporting Information

# Pyrochlore electrocatalysts for efficient alkaline water electrolysis

Javier Parrondo[a], Morgan George[b], Christopher Capuano[b], Katherine E. Ayers[b], and Vijay Ramani[a, *]

[a] Center for Electrochemical Science and Engineering, Department of Chemical and Biological Engineering, Illinois Institute of Technology, 10 W. 33rd St., Chicago, IL 60616

*Corresponding author's e-mail: ramani@iit.edu

[b] Proton Energy Systems, Wallingford, CT 06492, USA

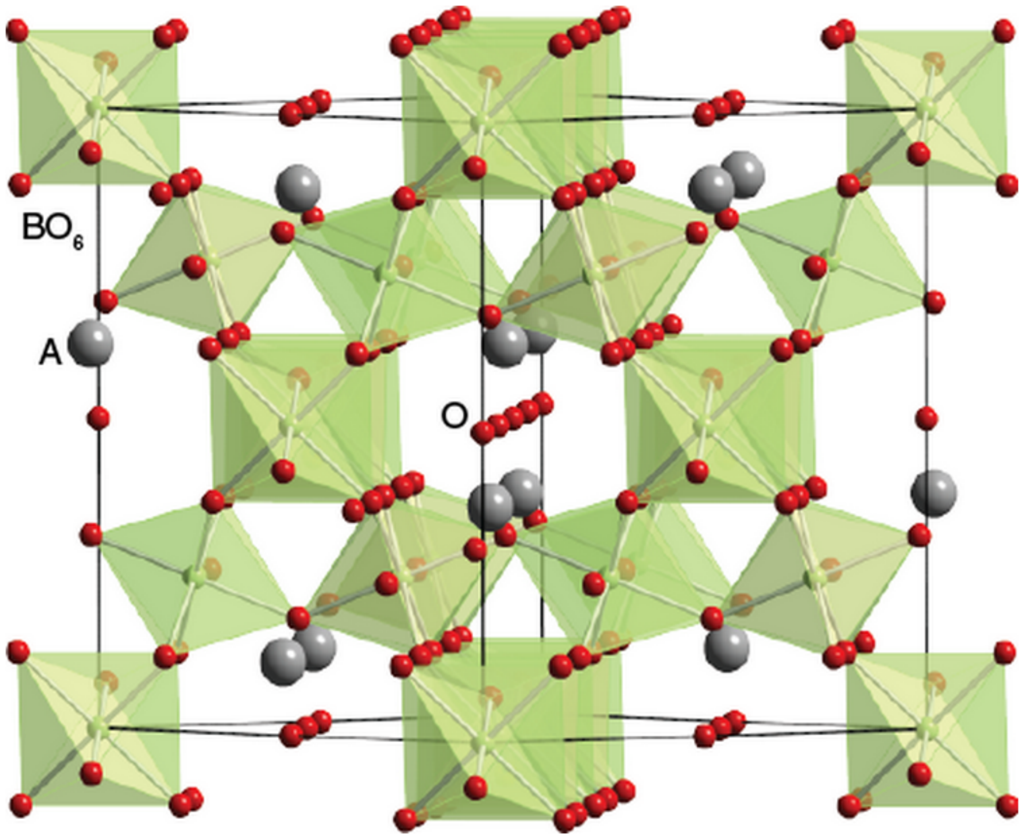

**Figure S1.** Crystalline structure of pyrochlores with general formula $A_2B_2O_{7-y}$.[1]

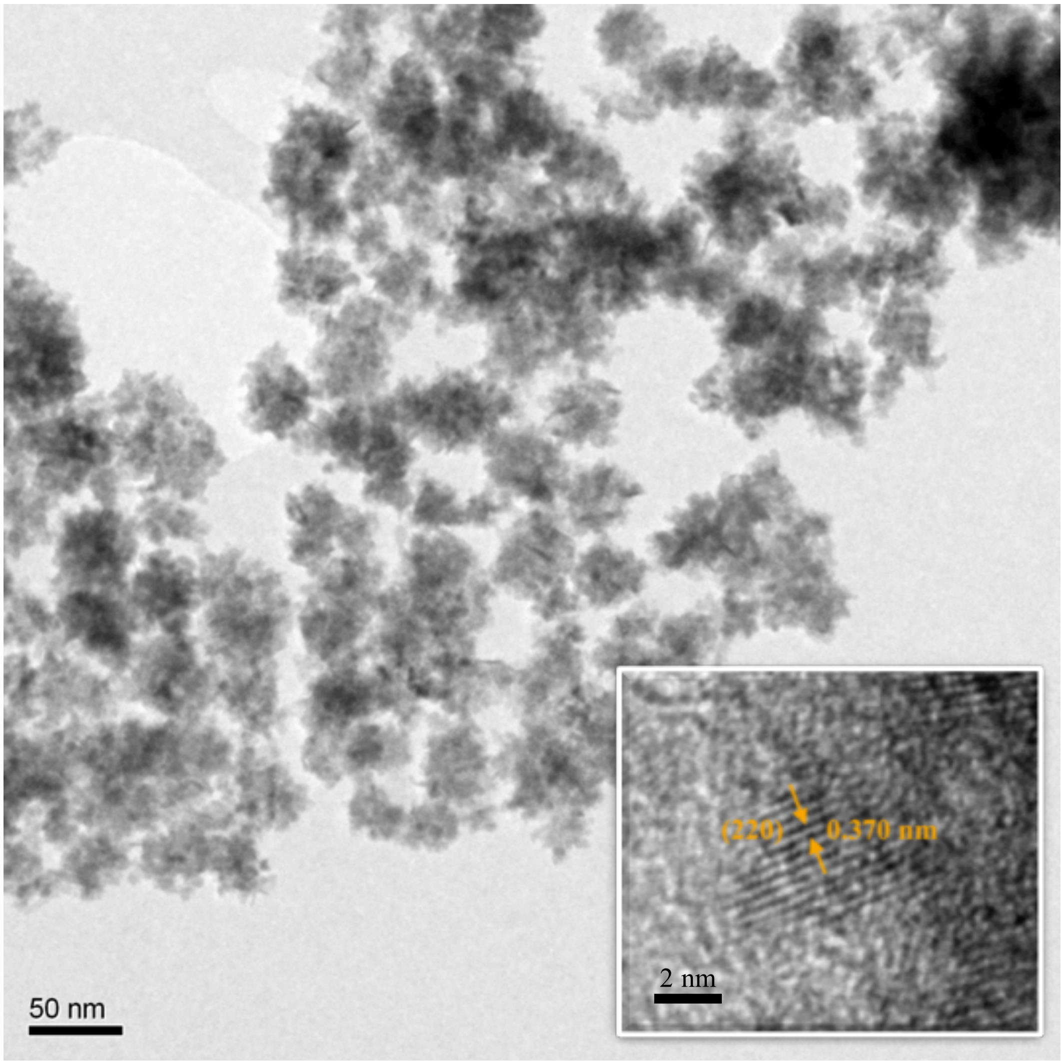

**Figure S2.** TEM micrograph of $Pb_2Ru_2O_{6.5}$ . The material showed particle-like aggregates of approximately 50-100 nm constituted of smaller particles glued together. The insert in the figure shows the Fresnel fringes for a particle demonstrating that some particles were crystalline.

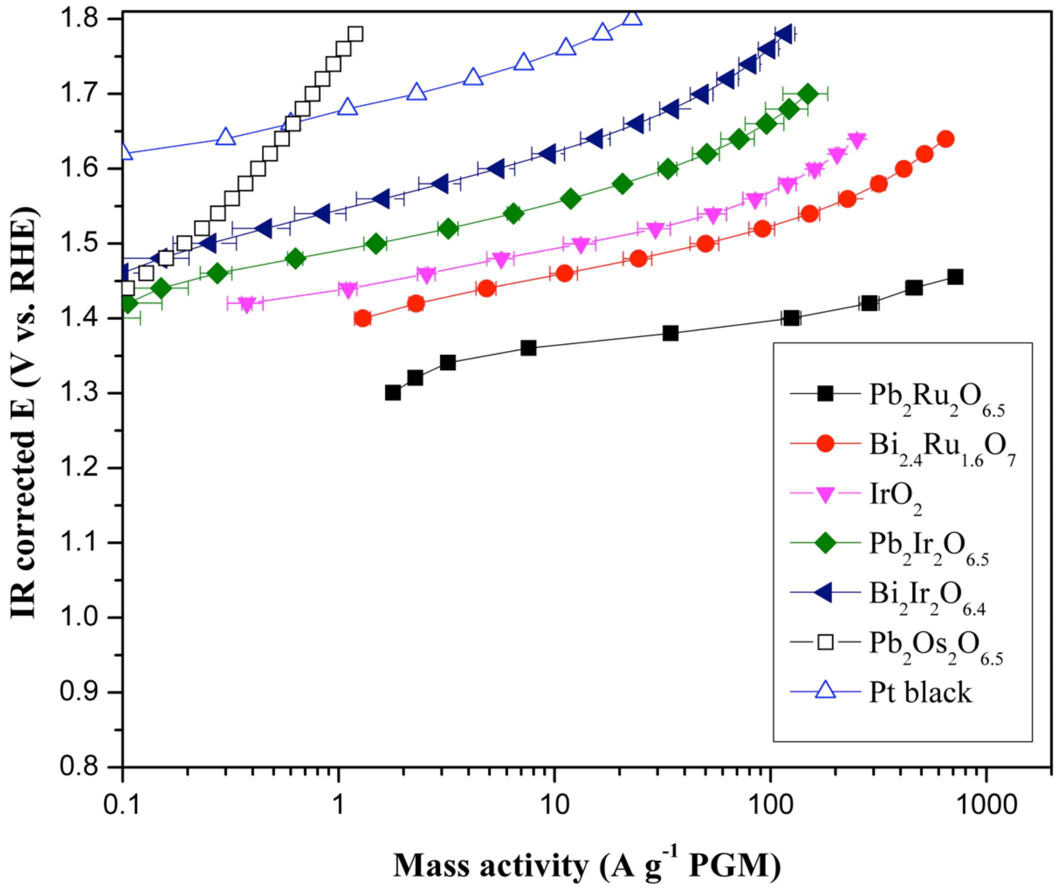

**Figure S3.** OER activities based on PGM loading of $Pb_2Ru_2O_{6.5}$, $Bi_{2.4}Ru_{1.6}O_7$, $Pb_2Ir_2O_{6.5}$, $Bi_2Ir_2O_7$, $Pb_2Os_2O_{6.5}$, $IrO_2$ and Pt black vs. IR corrected potential (from capacity-corrected positive-going scans at 5 mV $s^{-1}$ in 0.1 M KOH). Error bars represent standard deviations from at least three independently repeated measurements.

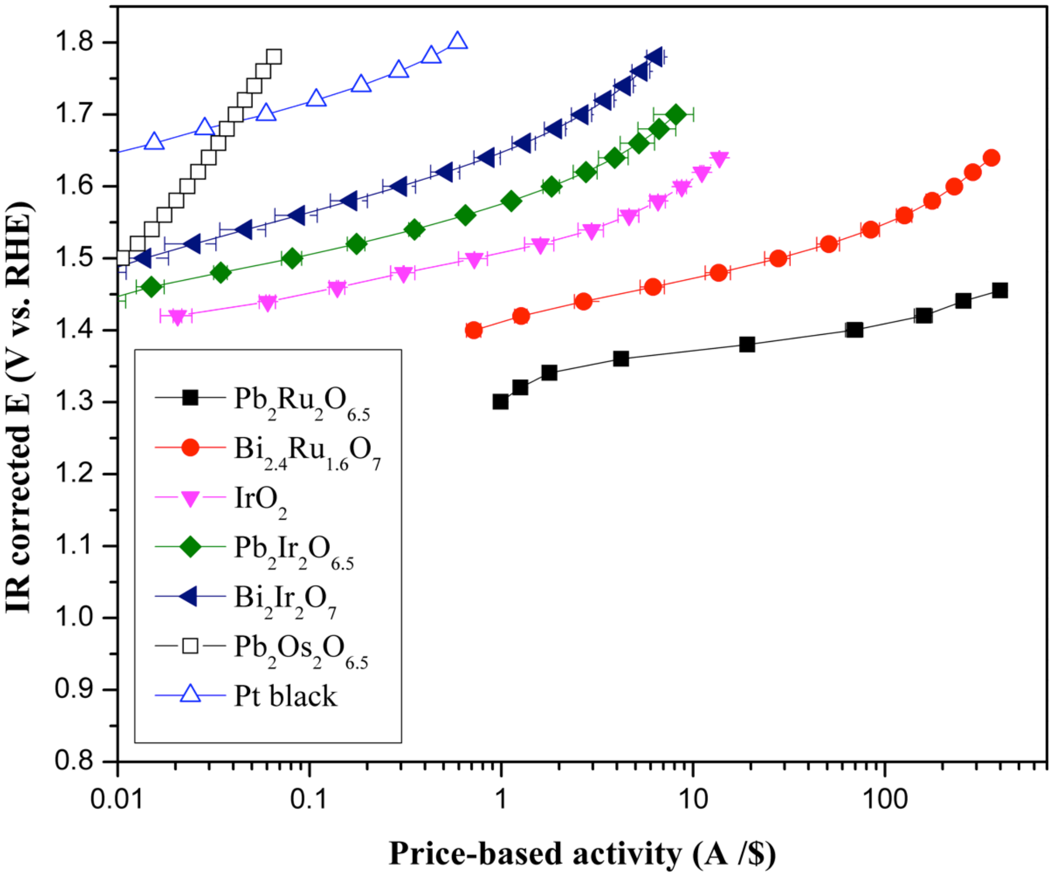

**Figure S4.** OER activities based on PGM spot prices (Feb 14, 2015) for $Pb_2Ru_2O_{6.5}$, $Bi_{2.4}Ru_{1.6}O_7$, $Pb_2Ir_2O_{6.5}$, $Bi_2Ir_2O_7$, $Pb_2Os_2O_{6.5}$, $IrO_2$ and Pt black vs. IR corrected potential (from capacity-corrected positive-going scans at 5 mV $s^{-1}$ in 0.1 M KOH). Error bars represent standard deviations from at least three independent repeated measurements.

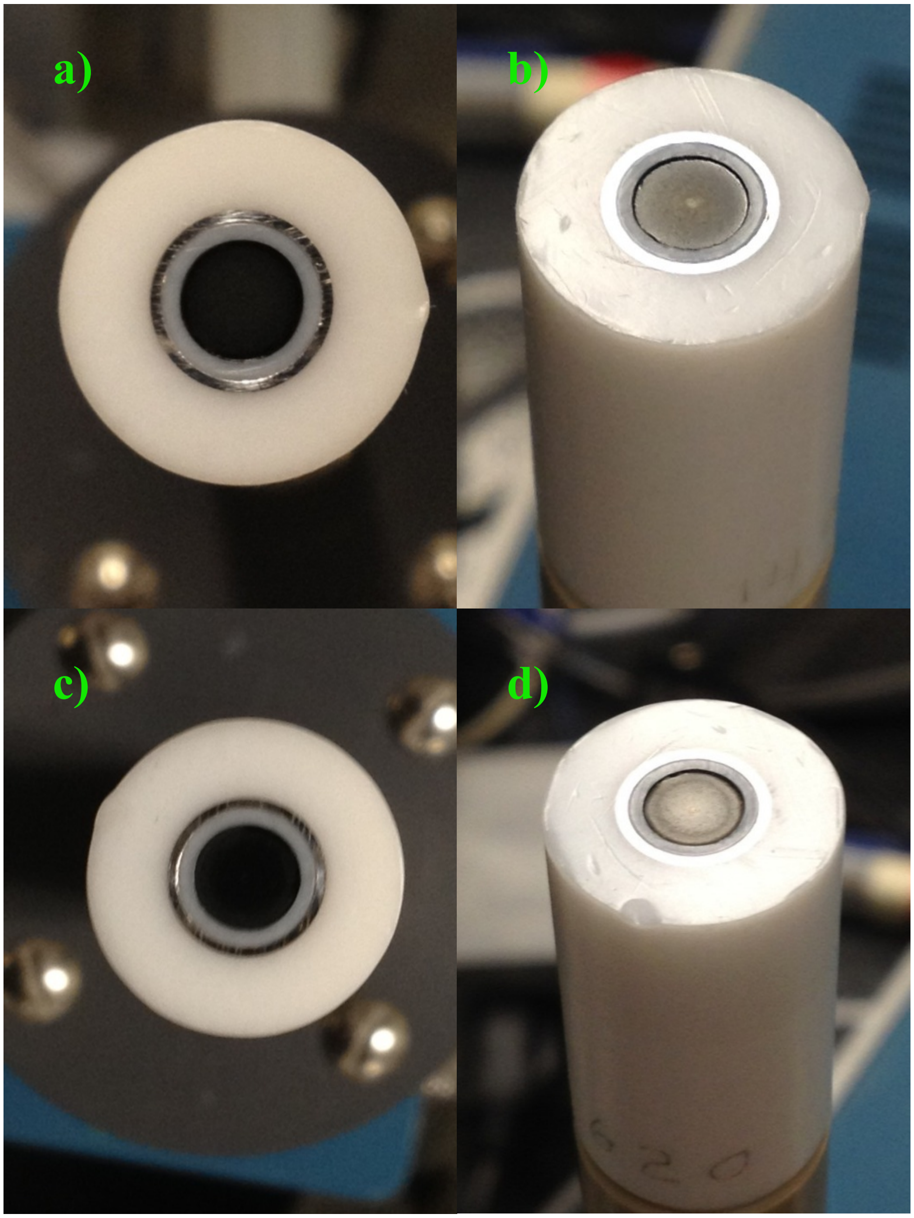

**Figure S5.** Typical appearance of the catalyst deposited onto the surface of the GC electrode before starting the OER experiment (a and b), and same electrode after the experiment was done (c and d). Pictures show a complete covered GC substrate and a smooth and uniform electrode; no degradation or partial disintegration of the electrode was observed after running the OER experiment.

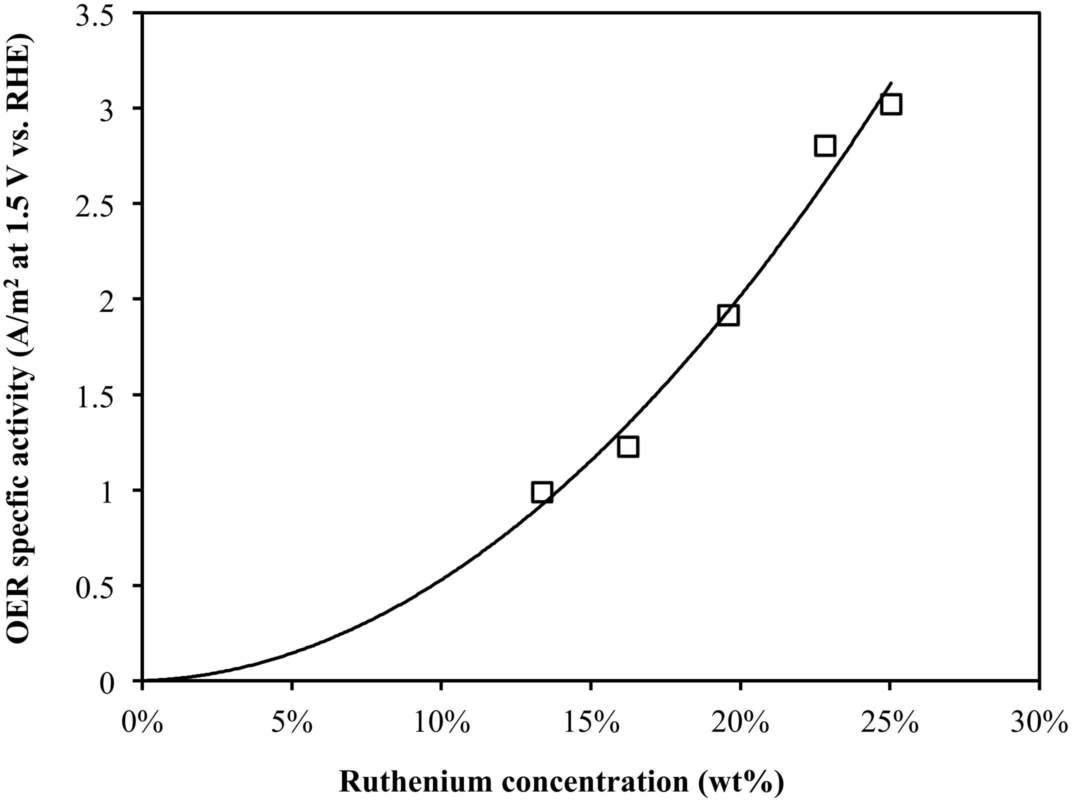

**Figure S6.** Specific OER activities (at 1.5 V vs. RHE) for lead ruthenate pyrochlores with varying ruthenium concentrations ($Pb_{2+x}Ru_{2-x}O_{6.5}$; x= 0, 0.3, 0.5, 0.7 and 0.9). Activities calculated from capacity-corrected positive-going scans at 5 mV $s^{-1}$ in 0.1 M KOH.

**Table S1**. Relationship between OER activity and d-band center and adsorbate (*s* or *p*)–metal *d*-coupling matrix element squared, $V^2_{ad}$ (properties were calculated using DFT for metallic surfaces).

| **Catalyst** | **B-cation** | **d band center* ($\varepsilon_d$, eV)** | **$V^2_{ad}$*** | **$i_m$ (A/g)** | **$i_s$ (A/m$^2$)** |
|---|---|---|---|---|---|
| **$Pb_2Ru_2O_{6.5}$** | Ru | -1.41 | 3.87 | 202±20 | 3.0±0.2 |
| **$Bi_{2.4}Ru_{1.6}O_{6.9}$** | Ru | -1.41 | 3.87 | 10±2 | 1.3±0.2 |
| **$Pb_2Ir_2O_{6.5}$** | Ir | -2.11 | 4.45 | 0.6±0.1 | 0.5±0.1 |
| **$Bi_2Ir_2O_{6.8}$** | Ir | -2.11 | 4.45 | 0.11±0.03 | 0.3±0.1 |
| **$Pb_2Os_2O_{6.5}$** | Os | **----** | 5.13 | 0.08±0.03 | 0.1±0.05 |

*Electronic properties of the metals taken from the paper of Hammer and Nørskov.[2]

**Determination of eg filling of Ru and Ir in pyrochlores.**

The average oxidation state of Ru in $Pb_2Ru_2O_{6.5}$ was estimated to be 4.5 (assuming all the Pb had an oxidation state of 2 and 6.5 oxygen atoms in the pyrochlore molecule), and hence the electronic configuration of the $Ru^{4.5+}$ can be written as Kr $4d^{2.5}$ $5s^1$. According to crystal field theory, the d orbitals split (in octahedral symmetry) into two sets of orbitals: t2g (lower energy, $d_{xy}$, $d_{yz}$, and $d_{zx}$) and $e_g$ (with higher energy, $d_{z2}$ and $d_{x2-y2}$). The 4d and 5d orbitals are more extended compared to 3d orbitals, and hence hybridization of the d and O2p orbitals is much more pronounced than the d-d orbital interactions, resulting in a large octahedral crystal field splitting. In general, for an octahedral complex, with strong field ligands or 4d/5d transition metal (Ru and Ir are 4d and 5d respectively) the electronic configuration is always low spin. We therefore assumed low spin configurations for our materials. In the case of $Pb_2Ru_2O_{6.5}$ we assume the following electronic configuration: $t_{2g}^{3.5}$ $e_g^0$ for our discussion.

For $Bi_{2.4}Ru_{1.6}O_{7-y}$ the amount of oxygen vacancies was reported to be ~0.1 and hence it can be represented as $[(Bi^{3+})_2]$ $[(Ru^{3.63+})_{2-0.4}$ $(Bi^{5+})_{0.4}]$ $O_{7-0.1}$.[3] Ruthenium ion has an average oxidation state of 3.63 resulting in electronic configuration $4d^{3.37}$ $5s^1$ ($t_{2g}^{4.37}$ $e_g^0$).[4]

Iridium has the following electronic configuration: Xe $4f^{14}$ $5d^7$ $6s^2$. $Pb_2Ir_2O_{7-y}$ and $Bi_2Ir_2O_{7-y}$ had oxygen vacancies (y) of 0.532 and 0.185 that result in average oxidation states (Ir) of 4.45 and 3.82 respectively.[5] These oxidation states result in the following electronic configurations: $t_{2g}^{4.55}$ $e_g^0$,and $t_{2g}^{5.18}$ $e_g^0$.

## References

1. The University of Liverpool, ChemTube 3D, http://www.chemtube3d.com/solidstate/SS-Pyrochlore.htm, Accessed March 9, 2015.
2. B. Hammer and J. K. Nørskov, in *Adv. Catal.*, ed. H. K. Bruce C. Gates, Academic Press, 2000, pp. 71-129.
3. G. Gulsun and B. J. Kennedy, *J. Electroanal. Chem.*, 1994, **368**, 235-239.
4. J. O. Bockris and T. Otagawa, *J. Electrochem. Soc.*, 1984, **131**, 290-302.
5. B. J. Kennedy, *Physica B*, 1998, **241-243**, 303-310.