Mendeleev Commun., 2015, **25**, 293–295

Mendeleev
Communications

Galvanic-displacement modification of Pd deposits with ultralow amounts of platinum and the electrocatalytic properties of the mixed catalyst

Boris I. Podlovchenko,* Tatyana D. Gladysheva and Alexander Yu. Filatov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 939 0171; e-mail: podlov@elch.chem.msu.ru

DOI: 10.1016/j.mencom.2015.07.022

The formation of the Pt^0_{Cu}(e.d.Pd) catalyst involves the displacement of palladium by platinum in addition to the displacement of copper adatoms.

In connection with the quest for highly efficient electrocatalysts for fuel cells, keen attention is paid to palladium catalysts modified with small amounts of platinum.[1–9] Platinum is deposited by both galvanic displacement (GD)[1–5,9] and chemical deposition.[6–8] The structures thus prepared are referred to as ‘core–shell’ structures. However, this term is often used only conditionally because here one deals with the excessive presence of Pt, as compared to Pd, in the upper layers of the catalyst rather than with a continuous platinum shell. Usually, the deposition of Pt on Pd by GD is preceded by the formation of a submono- or monolayer of adatoms of a non-precious metal (most often, Cu_{ad}).[1–5] However, is was shown recently[9] that, under certain conditions in solutions containing $PtCl_4^{2-}$ ions, the Pd surface layer can be enriched in Pt due to the direct displacement of palladium by platinum. According to published data, the mixed Pt–Pd catalysts exhibit high activity in the electrochemical reactions of oxygen reduction[1–6] and oxidation of methanol (MOR)[6–8] and formic acid (FAOR).[9] These results are of scientific and practical interest because Pd is a less expensive metal than Pt.

Earlier, we considered the properties of the electrolytic deposits (e.d.) of Pd and the adsorption of copper adatoms on them[10–12] and also the GD of a Cu_{ad} monolayer ($MLCu_{ad}$) on Pt deposits.[13,14] It was interesting to use the e.d.Pd–$MLCu_{ad}$(e.d.Pd)– $PtCl_4^{2-}$ system as a model when studying (i) the advantages of using GD for the synthesis of Pd–Pt catalysts with the ultralow content of Pt; (ii) the displacement of palladium-supported Cu_{ad} by platinum; and (iii) the characteristic structural and electrocatalytic properties of the surface layer on e.d.Pd modified by microamounts of Pt. The electrocatalytic activity of Pt^0(e.d.Pd) was studied with respect to MOR and FAOR.

All electrochemical measurements were carried out in a three-electrode cell with separate anodic and cathodic compartments. The reference electrode represented a reversible hydrogen electrode in the same solution (all the potentials E are shown in the RHE scale). Palladium was deposited on a Pt plate with $S_{geom} = 1$ cm^2 from a solution containing 1 wt% $PdCl_2$ + 0.5 M H_2SO_4 at $E_{dep} = 0.25$ V (to obtain stable characteristics, we always used a fresh solution portion for the deposition). The quantity of electricity passed at electrolysis corresponded to the deposition of ~1 mg Pd (this amount is sufficient that the contribution of the e.d.Pd/Pt interface can be neglected[15]). After repeatedly washing the cell from palladium ions with the supporting electrolyte solution (0.5 M H_2SO_4), the latter was changed for a copper-ion-containing solution (5 mM $CuSO_4$ + 0.5 M H_2SO_4) and the $MLCu_{ad}$ was formed at $E = 0.29$ V.[10,14] Then, the working compartment of the cell was washed with the supporting electrolyte solution in an argon flow; the circuit was opened, and the solution was changed for a deaerated solution of 2 mM K_2PtCl_4 + + 0.5 M H_2SO_4. After this, the transient of open-circuit potential E *vs.* τ was measured. Once the stationary potential was reached (E_{st}, $\Delta E/\Delta\tau < 2$ mV min^{-1}), the solution was sampled from the cell to be analyzed for the Pd content. For comparison, experiments were staged on bringing the solution of 2 mM K_2PtCl_4 + + 0.5 M H_2SO_4 into contact with e.d.Pd in the absence of Cu_{ad}. Below, the electrodes prepared by the GD of Cu_{ad} are referred to as Pt^0_{Cu}(e.d.Pd)/Pt and those prepared without copper displacement are designated as Pt^0(e.d.Pd)/Pt.

For all the electrodes, the electrochemically active surface area (EASA) was determined with respect to Cu_{ad}.[12,14] Note that, for the composite platinum–palladium electrode, the total surface of (Pt + Pd) was determined because the Cu_{ad} electrodesorption from these metals proceeds in close potential ranges. To determine the electrochemical activity of the test electrodes, the stationary polarization curves were measured in solutions of 0.5 M MeOH + + 0.5 M H_2SO_4 and 1 M HCOOH + 0.5 M H_2SO_4. All the currents were calculated per the EASA. The criterion of stationarity was the current variation at a fixed E by less than 2% per minute.

The insert in Figure 1 shows transients of open-circuit potential observed upon the contact of $PtCl_4^{2-}$ with either e.d.Pd in the presence of a $MLCu_{ad}$ or e.d.Pd without Cu_{ad}. Curve *1* demonstrates a well-pronounced arrest corresponding to the removal of Cu_{ad}. It is evident that the stationary potentials (E_{st}) established upon the contact of the platinous chloride solution with e.d.Pd in the presence (curve *1*, $E_{st} = 0.88\pm0.01$ V) and in the absence of Cu_{ad} on the surface (curve *2*, $E_{st} = 0.85\pm0.01$ V) are close. These E_{st} correspond to potentials of the beginning of oxygen adsorption on Pt and the total removal of Cu_{ad} from the surface of both Pt and Pd[10–14] according to the reaction

$$Cu_{ad} + PtCl_4^{2-} \rightarrow Pt^0 + Cu^{2+} + 4Cl^- . \qquad (1)$$

At the same time, after the removal of $MLCu_{ad}$ (curve *1*), E_{st} is substantially lower, as compared with polycrystalline Pt under analogous conditions (~920 mV).[13] This alone confirms that no continuous Pt^0 layer is formed on the surface of e.d.Pd.

Figure 1(*a*) shows CVA on the original e.d.Pd/Pt (curve *1*) and Pt^0_{Cu}(e.d.Pd)/Pt (curve *2*). The appearance of Pt on the Pd surface considerably changes the energy spectrum of hydrogen electrodesorption: the fraction of strongly bound hydrogen decreases. Moreover, the surface determined with respect to copper adsorption increases by a factor of ~1.3. The curve of Cu_{ad} electrodesorption also substantially changes: its complete removal from Pt^0_{Cu}(e.d.Pd) occurs at the higher E, as compared with e.d.Pd. This agrees with the higher potential of complete removal of Cu_{ad} from Pt, as compared with Pd.[11–13] It deserves mention that

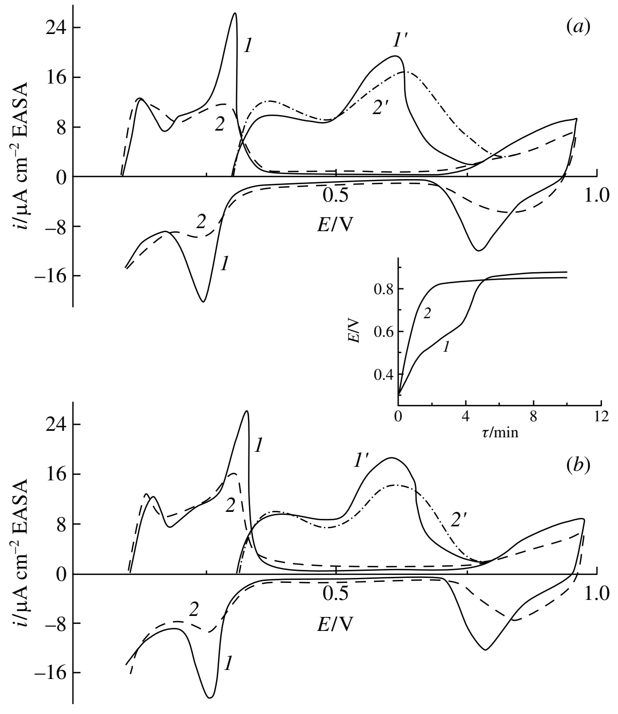

Figure 1 Potentiodynamic curves in 0.5 M H_2SO_4 on (*1*) e.d.Pd and (*2*) platinum-modified e.d.Pd: (*a*) Pt^0_{Cu}(e.d.Pd)/Pt; (*b*) Pt^0(e.d.Pd)/Pt. (*1*′, *2*′) curves of $MLCu_{ad}$ electrodesorption. Insert: transients of open-circuit potential at the contact of $PtCl_4^{2-}$ with (*1*) $MLCu_{ad}$(e.d.Pd) and (*2*) e.d.Pd.

the displacement of $MLCu_{ad}$ by platinum from the palladium surface to afford the Pt^0 monolayer should not be expected to induce any changes in the EASA because Pt and Pd have similar lattices with close parameters (a = 3.890 nm for Pd and 3.920 nm for Pt). The considerable increase in EASA allows us to assume that Pt is nonuniformly distributed on the surface of a porous Pd deposit.

An important result was obtained when a solution in which the $MLCu_{ad}$ was displaced by platinum was analyzed for palladium that was detected in this solution. This unambiguously suggests that, in addition to reaction (1), the following reaction occurs:

$$PtCl_4^{2-} + Pd \rightarrow Pt^0 + Pd^{2+} + 4Cl^-. \tag{2}$$

In the experiment with e.d.Pd with an EASA of ~57 cm^2, the solution after the removal of $MLCu_{ad}$ contained 14 μg Pd, which was assessed to correspond to the displacement of ~0.7 Pd monolayer.

At first glance, the removal of Pd by platinum according to reaction (1) contradicts the thermodynamics because the standard electrode potential of the reaction $PtCl_4^{2-}$ + 2e ↔ Pt + 4Cl$^-$ (E_1^0 = 0.740 V) is much lower than the standard potential of the reaction Pd^{2+} + 2e ↔ Pd (E_2^0 = 0.987 V). However, the equilibrium potential of the former reaction strongly depends on the concentration of chloride anions in the solution. Knowing the charge consumed in the $MLCu_{ad}$ desorption, we calculated the amount of displaced Pd according to reactions (1) and (2) and assessed the amount of Cl$^-$ anions that appeared in our experiments after the GD as ~2 μmol dm^{-3}. Based on the found Cl$^-$ concentration and [$PtCl_4^{2-}$] = 2 mmol dm^{-3}, the equilibrium potential of the reaction $PtCl_4^{2-}$/Pt was assessed as > 1.20 V, which resolves the seeming contradiction. Note that we failed to find any publications in which a considerable contribution of reaction (2) was taken into account when palladium was modified by platinum *via* Cu_{ad}.

In line with the observed effect of the partial displacement of Pd accompanying the displacement of Cu_{ad}, it was of interest to follow changes in the e.d.Pd characteristics upon its open-circuit contact with $PtCl_4^{2-}$ anions in the absence of both Cu_{ad} from the surface of Pd and Cu^{2+} from the solution. On the qualitative level, the adsorption characteristics of the Pt^0(e.d.Pd)/Pt electrode [Figure 1(*b*)] are similar to those found for Pt^0_{Cu}(e.d.Pd/Pt) [Figure 1(*a*)]. However, there are certain differences. The surface determined with respect to Cu_{ad} remained virtually the same. The complete removal of Cu_{ad} from the surface of Pt^0(e.d.Pd) occurred at lower anodic potentials, as compared with Pt^0_{Cu}(e.d.Pd) (0.75 and 0.85 V, respectively). The suppression of adsorption of strongly bound hydrogen on Pt^0_{Cu}(e.d.Pd/Pt) [curve *2*, Figure 1(*b*)] was somewhat weaker. The observed changes in the adsorption characteristics after the contact of e.d.Pd with $PtCl_4^{2-}$ suggest that, in the absence of Cu_{ad}, the Pt deposition also proceeds by reaction (2). Indeed, the ICP AES measurements with the original Pd deposit (S_{true} = = 70 cm^2) revealed the presence of 6 μg of Pd in solution after the contact of the deposit with $PtCl_4^{2-}$. This corresponds to the displacement of ~0.4 Pd monolayer. The approximate calculation of the Pt amount that could be deposited additionally due to a change in the total charge[16,17] of e.d.Pd as a result of the reduction of $PtCl_4^{2-}$ anions (assuming that ΔE = 0.6 V and the average capacitance of e.d.Pd ~ 40 μF cm^{-2} of the EASA) afforded 0.15 MLPt. Thus, the total amount of Pt deposited at the contact of e.d.Pd with $PtCl_4^{2-}$ is equivalent to ~0.5 monolayer, which is ~3 times lower than that for the displacement of $MLCu_{ad}$. The Pt content of the whole sample was 4.1 wt% or 2.2 at% for Pt^0_{Cu}(e.d.Pd) and 1.5 wt% or 0.8 at% for Pt^0(e.d.Pd), *i.e.*, one can really speak of modification of e.d.Pd with ultralow amounts of Pt.

Information on the morphology and structure of Pt^0_{Cu}(e.d.Pd)/Pt and Pt^0(e.d.Pd)/Pt was obtained by the SEM and XPS.† The SEM images show that the direct displacement of Pd by platinum [Figure 2(*a*)] induces no considerable changes in the dendrite structure of the original palladium deposit [the latter image is identical to Figure 2(*a*)]. At the same time, the deposition of Pt through the GD of a Cu_{ad} monolayer produces deposits with the different morphology: they become globular and denser [Figure 2(*b*)]. This obvious change in the deposit structure allows us to assume that, during the displacement, the reactions Cu_{ad} – 2e → Cu^{2+}, Pd – 2e → Pd^{2+} and $PtCl_4^{2-}$ + 2e → Pt^0 + 4Cl$^-$ are spatially separated to a considerable extent.[18] The review XPS spectra (Figure 3) for Pt^0_{Cu}(e.d.Pd)/Pt and Pt^0(e.d.Pd)/Pt are similar [with the exception of copper traces distinguishable in spectrum (*a*)]. According to XPS data, the Pt : Pd ratio in the surface layer (2–3 nm) is 0.32 Pt^0_{Cu}(e.d.Pd) and 0.11 for Pt^0(e.d.Pd). This well agrees with the above estimates of the surface coverage of e.d.Pd with platinum for two test composites.

Figure 4 compares stationary polarization curves of electrooxidation of MeOH and HCOOH on Pt^0_{Cu}(e.d.Pd)/Pt, Pt^0(e.d.Pd)/Pt, e.d.Pd and e.d.Pt, all calculated per square centimeter of EASA (for mixed deposits, $EASA_{Pt+Pd}$). In the electrooxidation of methanol, the specific activity of platinum-modified Pd deposits [Figure 4(*a*),

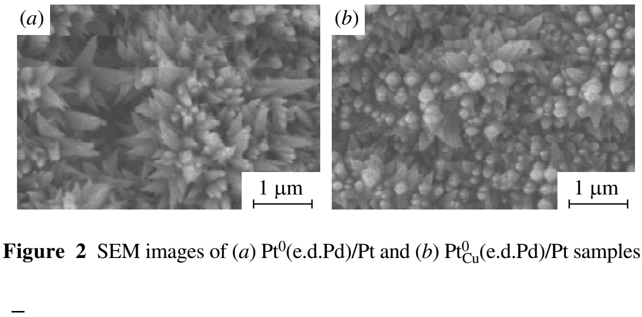

Figure 2 SEM images of (*a*) Pt^0(e.d.Pd)/Pt and (*b*) Pt^0_{Cu}(e.d.Pd)/Pt samples.

---

† The surface morphology of deposits was studied using a JEOL JSM-6490 LV scanning electron microscope. The amount of Pd passed to solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES). The surface layer composition was determined by XPS on a Kratos Axis Ultra DLD spectrometer.

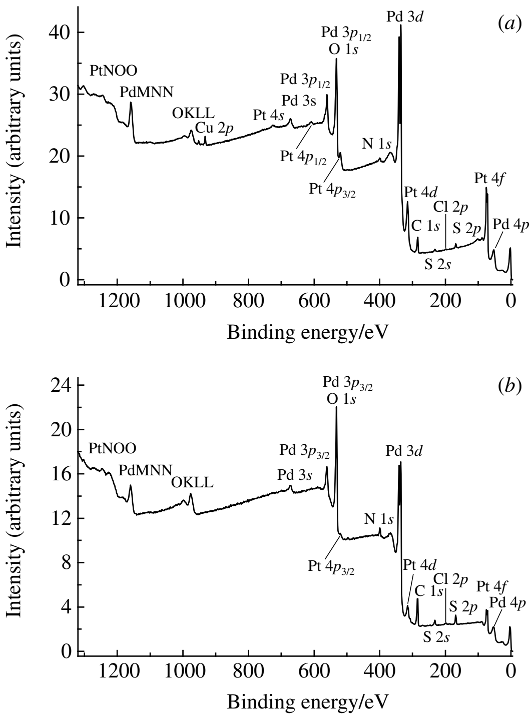

Figure 3 Review XPS spectra: (*a*) $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd)/Pt and (*b*) Pt^0(e.d.Pd)/Pt.

curves *1*, *2*] substantially exceeds that of e.d.Pd (curve *3*), as should be expected because of the very low Pd activity in this reaction. The specific activity in MOR increases as we pass from Pt^0(e.d.Pd) to $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd), which is explained by the larger part of catalyst surface occupied by Pt for catalysts prepared by GD of $\mathrm{Cu}_{\mathrm{ad}}$. Although a considerable amount of Pt equivalent to almost two monolayers is present on the surface of $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd), its specific activity is considerably lower, as compared with e.d.Pt on Pt (curve *4*). This agrees with the assumption on the non-uniform distribution of Pt on the surface of e.d.Pd and the presence of platinum-free areas on the Pd surface, which are inactive in MOR. Another reason can be the small size of Pt islets and/or particles (for MOR, a negative size effect was observed[19,20]). However, the specific mass activity of Pt (*i.e.*, for currents recalculated per mass unit) in $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd) is much higher as compared with e.d.Pt as such (at 0.6 V, ~5 and ~1.0 mA $\mathrm{mg}^{-1}_{\mathrm{Pt}}$, respectively). Such increase in the specific mass activity of Pt in the modified electrode can be due to the higher degree of dispersion of this Pt deposit (assuming in the first approximation the absence of any synergistic effect in the Pt–Pd system[14]). It is interesting that the specific mass activity of Pt with respect to MOR at 0.6 V found for the $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd) catalyst was close to that exhibited by the PtRu catalyst at 0.6 V.[20]

On the modified e.d.Pd, the specific currents of FAOR [Figure 4(*b*), curves *1* and *2*] are considerably lower compared to e.d.Pd (curve *3*). This seems reasonable taking into account the low activity of Pt in FAOR (curve *4*). Moreover, the specific activity of Pt^0(e.d.Pd) in FAOR is substantially higher than that of $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd). Apparently, this is mainly associated with the fact that more amount of platinum blocks better the palladium active sites at which the FAOR proceeds by the current-determining pathway *via* the single-site adsorption of HCOOH.[21,22] On the other hand, one can hardly expect the appearance of new active sites for FAOR on the platinum-modified e.d.Pd due to the close crystal structures of Pt and Pd.

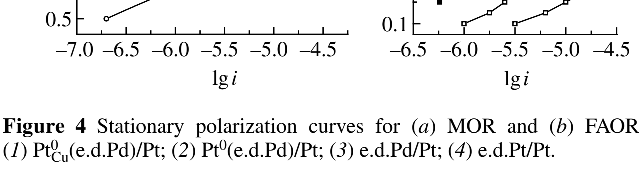

Figure 4 Stationary polarization curves for (*a*) MOR and (*b*) FAOR: (*1*) $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd)/Pt; (*2*) Pt^0(e.d.Pd)/Pt; (*3*) e.d.Pd/Pt; (*4*) e.d.Pt/Pt.

Note that all the above results for $\mathrm{Pt}^0_{\mathrm{Cu}}$(e.d.Pd)/Pt and Pt^0(e.d.Pd)/Pt were obtained for samples prepared by a procedure in which the contact time of $\mathrm{MLCu}_{\mathrm{ad}}$(e.d.Pd) and e.d.Pd with the PtCl_4^{2-} solution was limited to a time sufficient for the establishment of E_{st} (11–12 min). Recently, we have found that a 2-h contact of e.d.Pd with 2 mM $\mathrm{H_2PtCl_4}$ + 0.5 M $\mathrm{H_2SO_4}$ solution led to the removal of a Pd amount higher by a factor of 3 than that for the contact times used in this study. This confirms the absence of the formation of any dense Pt shell and the presence of at least partial spatial separation of the reactions of Pd ionization and Pt deposition.[18] The kinetics of palladium displacement by platinum deserves an independent study.

This work was supported by the Russian Foundation for Basic Research (project no. 15-03-03436) and, in part, by M. V. Lomonosov Moscow State University Program of Development.

References

1 K. Sasaki, H. Naohara, Y. Cai, Y. M. Choi, P. Liu, M. B. Vukmirovic, J. X. Wang and R. R. Adzic, *Angew. Chem. Int. Ed.*, 2010, **49**, 8602.

2 K. Sasaki, J. X. Wang, H. Naohara, N. Marinkowic, K. More, H. Inada and R. R. Adzic, *Electrochim. Acta*, 2010, **55**, 2645.

3 H. Naohara, Y. Okamoto and N. Toshima, *J. Power Sources*, 2011, **196**, 7510.

4 L. Hou and H. Qiu, *J. Power Sources*, 2012, **216**, 28.

5 W. Zhang, M. Wang, J. Chen, T. Romeo, A. T. Harris and A. I. Minett, *Electrochem. Commun.*, 2013, **34**, 73.

6 H. Zhang, Y. Yin, Y. Hu, C. Li, P. Wu, S. Wei and C. Cai, *J. Phys. Chem.*, 2010, **114**, 11861.

7 L. Wang, Y. Nemoto and Y. Yamauchi, *J. Am. Chem. Soc.*, 2011, **133**, 9674.

8 Y.-Y. Chu, Z.-B. Wang, Z.-Z. Jiang, D.-M. Gu and G.-P. Yin, *J. Power Sources*, 2012, **203**, 17.

9 M. Liao, Y. Wang, G. Chen, H. Zhou, Y. Li, C.-J. Zhong and B. H. Chen, *J. Power Sources*, 2014, **257**, 45.

10 B. I. Podlovchenko, E. A. Kolyadko and Sh. Lu, *J. Electroanal. Chem.*, 1995, **399**, 21.

11 A. V. Smolin, Yu. M. Maksimov and B. I. Podlovchenko, *Russ. J. Electrochem.*, 1997, **33**, 440 (*Elektrokhimiya*, 1997, **33**, 477).

12 Yu. M. Maksimov, A. S. Lapa and B. I. Podlovchenko, *Sov. Electrochem.*, 1989, **25**, 634 (*Elektrokhimiya*, 1989, **25**, 712).

13 B. I. Podlovchenko, U. E. Zhumaev and Yu. M. Maksimov, *J. Electroanal. Chem.*, 2011, **651**, 30.

14 T. D. Gladysheva, B. I. Podlovchenko and A. Yu. Filatov, *Mendeleev Commun.*, 2015, **25**, 56.

15 A. I. Fedorova and A. N. Frumkin, *Zh. Fiz. Khim.*, 1953, **27**, 217 (in Russian).

16 A. N. Frumkin, *Potentsialy nulevogo zaryada (Zero-Charge Potentials)*, Nauka, Moscow, 1981 (in Russian).

17 B. I. Podlovchenko and E. A. Kolyadko, *J. Electroanal. Chem.*, 2001, **506**, 11.

18 B. I. Podlovchenko, T. D. Gladysheva, V. A. Krivchenko, Yu. M. Maksimov, A. Yu. Filatov and L. V. Yashina, *Mendeleev Commun.*, 2012, **22**, 203.

19 Yu. M. Maksimov, B. I. Podlovchenko and T. L. Azarchenko, *Electrochim. Acta*, 1998, **43**, 1053.

20 S. H. Joo, K. Kwon, D. J. You, Ch. Pak, H. Chang and J. M. Kim, *Electrochim. Acta*, 2009, **54**, 5746.

21 M. Neurock, M. Janik and A. Wieckowski, *Faraday Discuss.*, 2009, **140**, 363.

22 B. I. Podlovchenko, Yu. M. Maksimov and K. I. Maslakov, *Electrochim. Acta*, 2014, **130**, 351.

Received: 24th November 2014; Com. 14/4510