

## Quantum-chemical study of the corrosion dissolution of platinum nanoclusters $Pt_nX_m$ in chloride containing water environment

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A model was proposed for corrosive dissolution of the surface of platinum binary nanoclusters  $Pt_nX_m$  ( $X$  – Cr, Fe, Co, Ni, Ru) with a shell structure in acid environment of low temperature fuel cells with the content of  $H_2O$ ,  $Cl^-$ ,  $OH^-$ ,  $H_3O^+$  (quantum-chemical method PM6 and DFT). Physico-chemical regularities are shown for our structural and energy degradation of the surfaces of shell structured binary nanoclusters  $Pt_{42}X_{13}$  of different composition under the influence of molecules and ions. It was shown that transition metals, forming the core of such binary nanoclusters, change essentially their adsorption abilities and resistance to corrosive dissolution, for example nanocluster  $Pt_{42}Co_{13}$  is very stable to the influence of chlorine hydrated ions  $Cl^-(H_2O)$  because of much lower adsorption heats on the cluster (275 kJ/mole) in comparison with pure platinum nanocluster (195.8 kJ/mole). It was depicted that on the surface of platinum binary nanoclusters in the environment of water molecules, oxygen atoms and hydroxyl ions the formation of complex  $[Pt(OH)(H_2O)_4]^+$  is possible, its departure activation energy being the largest for nanoclusters with cobalt and ruthenium in the row  $Pt_{55} < Pt_{42}Co_{13} < Pt_{42}Ru_{13}$ . We have established that chlorine ions local adsorption on the hydrated surface of platinum binary nanoclusters would block catalytic centers of their surface because of high adsorption activity of the ions both the dissolution of platinum surface atoms with the formation of complexes  $[H_2O(PtCl)]^{n+}$ , they have lower activation energy to delay the surface as compared with that of pure nanocluster  $Pt_{55}$  but the  $Pt_{42}Co_{13}$  must be excluded, whereas an opposite effect is observed. Thus the surfaces of nanoclusters  $Pt_{42}Co_{13}$  and  $Pt_{42}Ru_{13}$  with the shell structures are convenient to lower degradation in acid environment with the content of water molecules, oxygen atoms and hydroxyl ions, while the nanocluster  $Pr_{42}Co_{13}$ , beside this, is stable to the influence of chlorine hydrated ions in comparison with pure platinum nanocluster.