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Role of oxides in the electrochemical dissolution of Pd and its alloys

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Section S1

All electrochemical studies were carried out in a three-electrode cell with separate anodic and cathodic compartments. For solutions, we used the following reagents: $HClO_4$ (“Sigma-Aldrich”), $PbCO_3$ and H_2SO_4(“puriss p.a.”), $PdSO_4$, $CuSO_4$ and $PdCl_2$ (“Aldrich”), H_2O cleaned in the Milli-Q system. $Pb(ClO_4)_2$ was synthesized by the reaction of $PbCO_3$ with $HClO_4$. Solutions were cleaned from oxygen by durable bubbling of Ar (99.99). During electrodeposition, the solution in working compartment of the cell was stirred by a magnetic stirrer. The electrochemical measurements were carried out by means of potentiostats R30IM (“Elins”, Russia) and P-5827 (Russia).

The codeposition of Pd and M(Pb,Cu) was carried out onto plates of polycrystalline gold (pc Au) with the geometrical surface of 0.8 cm^2 from solution of 0.7 mM $Pd(ClO_4)_2$ + 5 mM $PdCl_2$ + 0.1 M $HClO_4$ and 1 mM $PdSO_4$ + 5 mM $CuSO_4$ +0.5 M H_2SO_4 at potential (E_{dep}) 100 and 400 mV, accordingly. The thickness of the deposits was ~ 0.4 µm (PdPb) and ~0.6 µm (PdCu). Pd electrodeposits used for comparison were deposited from 5 mM $PdCl_2$ + 0.1 M $HClO_4$ and 1 mM $PdSO_4$ + 0.5 M H_2SO_4 under the same conditions as for e.d. PdM.

The volume composition of deposits was determined by ICP-AES (inductively coupled plasma atomic emission spectroscopy) method (confidence interval ±10%); their surface composition was found from XPS (X-Ray photoelectron spectroscopy) spectra collected by means of spectrometer Axis Ultra DLD, Kratos (monochromic AlKα radiation with analyzer energy of 160 eV). The corresponding data are given in the table.

Table S1 Volume and surface composition of e.d. PdPb and PdCu

Sample	Analytical method	Pd, at. %	Pb, at. %
e.d. PdPb	AES-ICP	71	29
	XPS	78	22
e.d. PdCu	AES-ICP	81	19
	XPS	79	21

Section S2

The approximate estimate of the contribution of current of electrodissolution of Pb and Cu into the total charge when the potential is scanned from 0.7 to 1.25 V in curves of Fig. 3 was obtained with the use of data of Table 2. The dissolution currents are very low which allows assuming that they are kinetic currents and do not depend on the potential scan rate *v*. Hence, the integral charge consumed in leaching out of metals from alloys in this potential interval should be directly proportional to the time it takes to pass this interval, i.e., inversely proportional to *v*. Then, for the $PdPb_{100}$ deposit at v = 20 mV/s [Figure 3(*a*)] we can expect the dissolution of Pb to be 10 times weaker as compared with $v = 2$ mV/s (Table 2), *i.e.*, the maximum dissolution is ~5 µg. This amount of lead corresponds to the charge of 4.6 mC, whereas the deposition of a monolayer of O_{ads} requires 0.42 mC/cm^2 x 60 cm^2 =25.2 mC (60 cm^2 is the average value of the true surface of PdPb deposits under discussion).[1] Hence, the contribution of the lead dissolution current to the total anodic charge is ~15%. The analogous calculation for PdCu [Figure 3(*b*)] gave the contribution of copper dissolution current less than 15%.

1. B. I. Podlovchenko, Yu. M. Maksimov, D. S. Volkov and S. A. Evlashin, *J. Electroanal. Chem.*, 2020, **858**, 113787.