ELECTROCHEMISTRY

Dependence of the underpotential shift of metals cathodic deposition tellurium on the Gibbs energy of metal telluride formation

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Metal adlayer on a foreign substrate is an important intermediate product in the electrochemical layer-by-layer assembly of nanostructured materials [1–2]. The adlayers are formed by underpotential deposition (UPD) that is a cathodic reduction of the corresponding metal cations above the reversible potential $E(\text{Me}^{z+}/\text{Me})$. The underpotential shift characterizing the difference between the potential of UPD (E_{UPD}) and $E(\text{Me}^{z+}/\text{Me})$, has been known to depend linearly on the difference of the work functions of the substrate and the deposited metal in the UPD of metals on foreign metals [3]. The UPD of metals on tellurium shows much similarity with the UPD of metals on a foreign metal electrode in cyclic voltammetry, with few significant differences. The UPD on tellurium is more irreversible and the underpotential shift of the deposition potential shows no correlation with differences in the work functions of the metal that is deposited underpotentially and the substrate material. In the investigation of the UPD peculiarities on tellurium with voltammetric and nonstationary impedance techniques, we have derived a correlation of the UPD shift with the free energies of formation of the corresponding metal tellurides which is helpful for predicting UPD shifts in those adlayer deposition processes on tellurium that do not give clear voltammetric response of UPD for different reasons. Different methods of the UPD shift derivation from voltammetric data and potentiodynamic electrochemical impedance spectroscopy will be also discussed in the report.
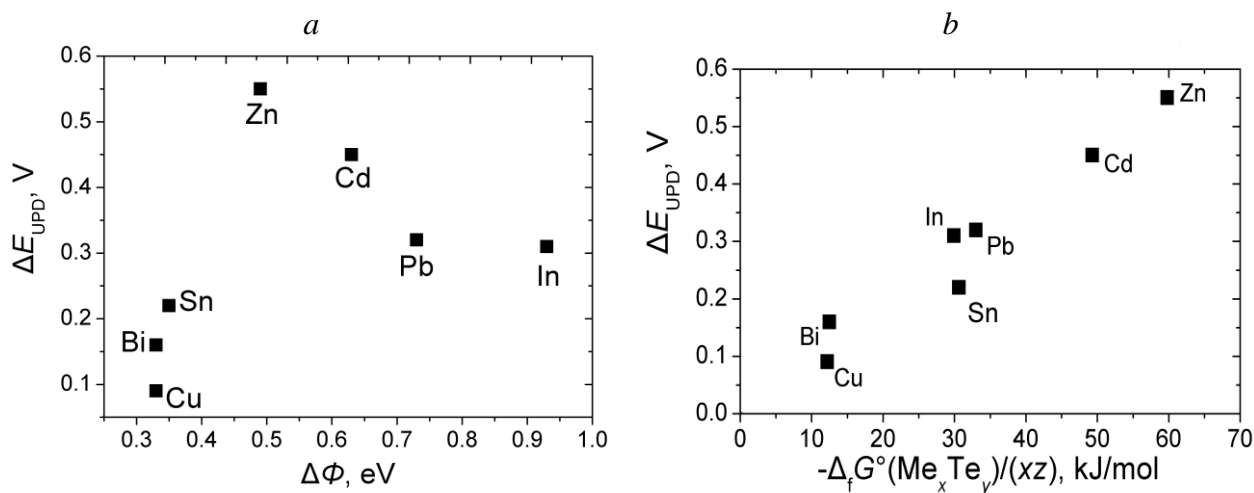

Fig. Underpotential shift versus (*a*) the work function difference $\Delta\Phi$ of tellurium and metal, (*b*) normalized Gibbs energy of metal telluride formation

References
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