Electroreduction properties of nanostructured WO_3-intercalated copper catalysts

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We demonstrate that the tungsten(VI)-oxide-intercalated nanostructured copper sites exhibit unique electrocatalytic properties toward electrochemical reductions of inert inorganic reactants, such as carbon dioxide, oxygen, nitrate(V), nitrate(III) and bromates(V). In particular, evidence has been provided that hierarchically deposited films (on glassy carbon) of copper(I) oxide decorated with tungsten(VI) oxide nanowires and, subsequently, subjected to electroreduction and voltammetric conditioning to generate hybrid Cu/WO_3 catalyst can be successfully utilized to drive reduction of carbon dioxide (saturated solution, concentration, ca. 0.033 mol dm^{-3}) in a fairly strong acid medium of 0.5 mol dm^{-3} H_2SO_4. Here formation of the partially reduced tungsten oxides (H_xWO_3 and WO_{3-y}) is accompanied by consumption of protons and sorption of hydrogen, and it tends to inhibit hydrogen evolution by shifting the proton discharge toward more negative potentials. Our observations are consistent with the view that copper is irreversibly trapped within the network of WO_3 nanowires. The dispersed metallic copper sites seem to facilitate electron transfers and charge distribution in the catalytic layers. Among important issues are the capacity of copper-containing partially reduced tungsten oxides to induce reductions of nitrates, bromates and oxygen in acid medium. On mechanistic grounds, the existence of hydrogen-rich partially-reduced tungsten oxides, H_xWO_3, which contain large population of delocalized electrons and monoatomic H, or coexisting protons and electrons, $H^+ + e^-$, is likely to induce hydrogenation of nitrogen oxo species, followed by protonation, in the vicinity of Cu to form ammonia-type products. The hybrid Cu/WO_3 system, is also characterized by improved durability, relative to pristine Cu_2O-dervided copper, as evident from electroreductions under chronoamperometric conditions. Our research aiming at optimization the material's activity and selectivity have also concentrated on application of mixed oxides, e.g. WO_3-ZrO_2. Finally, the present study demonstrates the usefulness of certain diagnostic electroanalytical approaches, such as ultramicroelectrode-based sensing, chronocoulometric probing of the diffusional-type charge propagation dynamics, or voltammetric stripping and monitoring of small organic or inorganic molecules as electroreduction products

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