Enhanced Catalytic Activity Induced by Ceria Nanotubes for Electro-oxidation of Methanol

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Nano-structured ceria-based materials are increasingly gaining attention for electro-oxidation of methanol due to the capability of ceria to act as a promoter for the preferential oxidation of CO to CO_2. Frequently, ceria nanotubes have been fabricated using hard templates such as carbon nanotubes and porous alumina. However, the diameters of these ceria nanotubes are typically in the range of 200 to 1000 nm, too large to have appreciable impact on their catalytic properties. Here, we report the synthesis of ceria nanotubes with diameters ranging from 50 to 160 nm and their electrochemical performance as a support of Pt nanoparticles for electro-oxidation of methanol. Ceria was formed on the surface of functionalized carbon nanotubes by a hydrothermal method obtaining a series of ceria/carbon nanotubes. The carbon template was completely removed by heating in air resulting in the formation of pure single-crystalline ceria nanotubes. The electrochemical performance was evaluated by cyclic voltammetry in 0.5 M H_2SO_4 and CH_3OH solution. Both, ceria-carbon and single-crystalline ceria nanotubes showed higher stability at anodic potentials than commercial carbon-Vulcan materials. The incorporation of Pt resulted in the formation of $Ce_{1-x}Pt_xO_{2-\delta}$ solid solution. The $Ce_{1-x}Pt_xO_{2-\delta}$-carbon nanotubes showed higher performance in methanol oxidation than commercial Pt/C-Vulcan or Pt/CeO_2 nanoparticles. Thus, the use of ceria nanotubes as a support promotes not only high activity towards methanol oxidation but also stability in the anodic region allowing the direct oxidation of methanol to CO_2. The XPS investigations showed that the Ce^{3+} ion number is about 10% of total cerium ion number, which may be responsible for the high performance of the $Ce_{1-x}Pt_xO_{2-\delta}$-carbon nanotubes.