

Coloration Mechanisms of Sol-Gel NiO-TiO₂ Layers Studied by EQCM

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An electrochemical quartz crystal microbalance was used as a sensitive detector to analyse the mass changes occurring during the coloration/bleaching processes of sol-gel NiO-TiO₂ electrochromic layers. Double layers were deposited on gold coated quartz crystal electrode and sintered at 300 °C in air. The electrochemical process was studied in KOH electrolyte in the potential range -0.4 to +0.57 V vs. SCE during 650 CV cycles. The current density, charge and mass were found to increase with cycling. The shape of the mass spectrum is rather complex and changes continuously by cycling. The mass of the layer increases after each cycle slowly up to about the 150th cycle then it increases strongly after about the 250th cycle. It passes through a maximum around the 570th cycle with high amplitude variation within each cycle and then decreases fast without drastic change of the cathodic charge. Finally a complete breakdown occurs around the 650th CV cycle impeding to record any further mass variation. The study is divided in two typical regions where the mechanism of coloration is found to change by cycling. During the first 150 CV cycles, the reversible change of the mass with the charge (increase in the anodic range for $V > 0.35$ V vs. SCE and decrease in the cathodic range for $V < -0.2$ V) was related to exchange of OH⁻ groups that involves a change of the oxidation state of Ni from 2⁺ to 3⁺ and vice versa leading to coloration and bleaching processes respectively. For further cycling a model is proposed taking into account the incorporation of $K(H_2O)_n^+$ ions in the hydrated structure of the layer. The irreversible increase of both the mass and charge exchanged during each cycle is interpreted as due to an increase of the amount of Ni(OH)₂.