SELECTIVE ELECTROLESS VAPOR DEPOSITION OF CONDUCTIVE, CATALYTICALLY ACTIVE, HYDROUS RUTHENIUM OXIDE THIN FILMS

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Ruthenium dioxide is a chemically diverse material used in numerous commercial applications. Anhydrous RuO_2 exhibits low-temperature stability and metallic conductivity on the order of 10^4 S•cm^{-1}, so it is used as a diffusion barrier and bottom electrode and in electronic components and as a low-temperature resistor. The hydrous form of RuO_2, denoted as $RuO_2•xH_2O$, RuO_xH_y, and/or RuO_2, is a mixed proton and metallic conductor (1). The metallic conductivity of the ruthenium oxide allows rapid electronic transport and the structural water allows proton insertion (2), making the material an ideal pseudocapacitor or ultracapacitor (3). $RuO_2•xH_2O$ is also an active component of the electrocatalysts used for chlorine generation via brine electrolysis at dimensionally stable anodes (DSAs) (4) and for methanol oxidation in direct methanol fuel cells (DMFCs) (5,6).

We have developed a process to prepare $RuO_2•xH_2O$ thin films on selective surfaces at ambient temperatures and pressures by the electroless vapor deposition of RuO_4(g) (7). RuO_4(g) is generated on demand and in situ from aqueous Ru–oxidant solutions of a commercial precursor, such as $RuCl_3•xH_2O$ (Alfa) or $RuO_2•xH_2O$ (Alfa), mixed with oxidizers having a standard potential > 1.3 V vs. a normal hydrogen electrode. The RuO_4(g) is reduced to a $RuO_2•xH_2O$ solid when it contacts selected functional groups and surfaces including: alcohols (–C–OH), thiols (–SH), amine/amides ($–NH_x$), and clean metal surfaces. The $RuO_2•xH_2O$ films continue to grow via the autocatalytic decomposition of RuO_4(g) on the as-deposited $RuO_2•xH_2O$.

$RuO_2•xH_2O$ films are uniformly deposited on substrates that have been surface-modified with or already contain the RuO_4–reactive functional groups summarized above. As-prepared $RuO_2•xH_2O$ films on Ti and carbon have excellent catalytic activity for chloride oxidation. The electrocatalytic activity of 10-nm-thick films on Ti decreases as the films are heated at 150 °C and 400 °C.

The selectivity of the $RuO_2•xH_2O$ deposition process is exemplified in Fig. 1 which shows the result when RuO_4(g) contacts 100-µm-wide polyimide strips on a silicon substrate. Both X-ray photoelectron spectroscopy and energy dispersive spectroscopy show that the polyimide strips are coated with $RuO_2•xH_2O$, while the SiO_2-passivated Si remains free of Ru. The SiO_2 scale on the Si increases in thickness during the deposition of the films.

$RuO_2•xH_2O$ films can be deposited on the perflurosulfonic membrane, Nafion, after it is surface-modified with p-aminophenol. The Nafion-supported $RuO_2•xH_2O$ films are electrocatalytically active for methanol oxidation after being decorated with electrodeposited Pt (8). Half-cell voltammetric measurements indicate that 1-µm-thick $RuO_2•xH_2O$ films on Nafion with approximately 10 ng Pt/cm^2 can function directly as anodes in DMFCs. We are also evaluating the performance of the $RuO_2•xH_2O$ films on Nafion as barriers to methanol crossover in DMFCs.

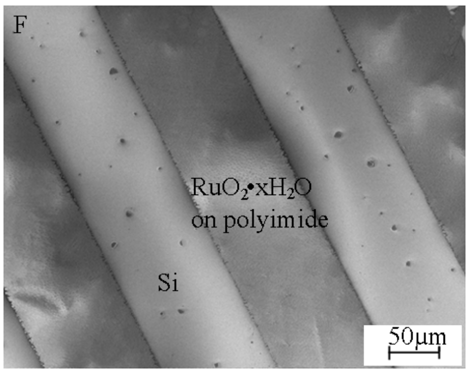

Figure 1. SEM micrograph of a 1-µm-thick $RuO_2•xH_2O$ thin film selectively deposited on polyimide trenches from RuO_4(g). No $RuO_2•xH_2O$ is present on the SiO_2-passivated silicon (light 100-µm wide lines).

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