

Electrodeposition of Y_2O_3 -Au composite coatings for SOFC interconnects: *in situ* monitoring of film growth by surface enhanced Raman spectroscopy

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In this paper, the authors report *in situ* surface enhanced Raman spectroscopy (SERS) experiments carried out during the electrochemical deposition of Y_2O_3 /Au from chloride salts dissolved in hydroalcoholic solutions containing chitosan as a binder. This composite was recently proposed by the authors as an electronically conducting coating able to protect AISI 430 interconnects from hot corrosion in SOFC cathodic environment. Dynamic SERS spectra were obtained during galvanostatic electrodeposition, showing peaks in the typical Raman shift range of M-O stretching and bending vibrations that have been tentatively assigned on the basis of quantum-chemical computations. The time dependence of the spectral features can be followed with a simple kinetic model accounting for the pH transient occurring in the catholyte.

Keywords: Electrodeposition, Composite, Au, Ytria, SOFC, SERS

Introduction

Ceramic electrodeposition (CED) is a relatively novel approach to the fabrication of functional coatings. In the last decade, this technique has been gaining increasing momentum in both fundamental studies and industrial research. This approach can be used for the growth of single- and multi-material films and exhibits a remarkable degree of flexibility. Ceramic electrodeposition requires simple and inexpensive equipment and it is a cost-effective fabrication route for ceramics, also allowing deposition of uniform films on complex-shaped substrates.¹⁻⁴ By this method, ceramic coatings are precipitated at an electrode from precursor salt solutions, via electrochemically mediated flocculation of colloidal particles.²

Electrodeposited ceramics and ceramic based composites have been proposed for several applications,¹ ranging from biomedical⁵⁻⁹ to electronic¹⁰⁻¹³ and from mechanical to catalytic.^{14,15} A particular field, to which this approach is expected to give unique results, is the fabrication of materials resistant to high temperatures for fuel cell applications, especially the solid oxide fuel cell (SOFC),¹⁶⁻²³ and to a lesser extent the molten carbonate fuel cell (MCFC).^{24,25} Some researchers have demonstrated the possibility of synthesising the

perovskite oxides used as SOFC cathodes, such as $LaMnO_3$ ²² and $LaCoO_3$.¹¹ The authors have demonstrated the possibility to obtain yttria stabilised zirconia/NiO composite films as SOFC anodes.²³ Ceramic electrodeposition has also been used to fabricate protective layers for some fuel cell components: (i) the growth of $La_{1-x}M_xCrO_3$ (M=Ca, Sr) thin films is described by Konno *et al.*,^{26,27} as a protective coating against high temperature oxidation; (ii) Zhitomirsky²¹ proposed CeO_2 and $Ce_{1-x}Gd_xO_{2-y}$ as interlayers preventing the degradation of the electrode/electrolyte interface and ensuring lower contact resistance for both SOFC anodes and cathodes; (iii) CoO coatings produced by electrochemical potentiostatic deposition in aqueous solution of $Co(NO_3)_2$ were used to protect the NiO cathode of MCFCs.^{24,25,28} These coatings have been reported to enhance the MCFC efficiency and to reduce the possibility of short circuiting by growth of Ni dendrites, in fact $LiCoO_2$ is significantly less soluble than NiO in molten carbonates.

Interconnect durability issues are currently believed to be the single most critical source of SOFC cell degradation, crucially limiting the operating lifetime. A method of reducing these disadvantages is to coat the surface of the metal with an electronically conductive ceramic protective film. Recently, mixed Mn-Co oxide coatings have been fabricated by anodic electrodeposition from Mn^{2+} and Co^{2+} sulphate baths.²⁹ Good performances were reported with Y_2O_3 or mixed yttrium/cobalt oxide coatings.³⁰ Wei *et al.*³¹ electrodeposited composite yttria-Ag coatings from Ag^+ and Y^{3+} nitrate solutions by a multiple-step approach, as well as praseodymia coatings from a chloride bath

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