

Kinetic studies of sol-gel formed Ni and Ni-Co oxide films

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Introduction

There has been a significant amount of interest in the past in the charge transfer kinetics of Ni oxide based materials, primarily due to their application as cathodes in secondary batteries. Co has been found to be a particularly useful additive, resulting in higher electrode charge capacities. Both Co and mixed Ni-Co oxide materials have also been investigated as promising catalysts for the oxygen evolution reaction (OER). These oxides have been synthesized in the past by the anodic oxidation of Ni, by cathodic precipitation, electron beam evaporation, chemical deposition, spray pyrolysis, and more recently, using sol-gel methods [1-3]. The latter approach appears to be very beneficial, due to the high surface areas achieved, the wide range of variables allowing for property optimization, and the overall ease of synthesis and film formation.

In alkaline solutions, the Ni(II)/(III) redox process is accompanied by the injection/expulsion of OH⁻, as well as Na⁺ and water, as shown by recent quartz crystal microbalance studies [3]. The involvement of the Na⁺ counter ion is also in agreement with the unusual ca. -90 mV pH dependence of the Ni oxide reaction. In the present work, the kinetics of the redox reaction of sol-gel formed Ni and 50:50 Ni-Co oxide films have been investigated using a range of electrochemical techniques.

Experimental

Ni, Co and mixed Ni-Co sol-gel (SG) solutions were prepared as described elsewhere [1]. The SG films were formed by dip-coating Pt foil substrates (0.3 – 0.8 cm²) at a constant withdrawal rate (1 to 60 cm/min) and drying at temperatures between 100 and 400°C for various periods of time, from 15 min to 1 hour. The SG films were equilibrated by soaking in 1 M NaOH overnight prior to the onset of electrochemical measurements.

Results and Discussion

The cyclic voltammetric response of both pure Ni and 50:50 Ni-Co oxide films in 1 M NaOH is relatively symmetrical with respect to the anodic vs. cathodic peak shape. However, the redox potential for the Ni-Co oxide is ca. 150 mV more negative than for pure Ni oxide, the charge density is higher (all other factors kept constant) and the peaks are broader. Also, the anodic and cathodic peaks are separated, even under reversible (current proportional to sweep rate) conditions.

In order to probe the redox kinetics of these films, chronoamperometric experiments were carried out. The *i/t* response of the SG-formed Ni oxide films

exhibited some unusual properties. The cathodic transients displayed the characteristic decay of a diffusion controlled process, while the anodic transients showed an abnormal current maximum. When the film conductivity is increased with the addition of Co, the anodic maximum almost disappears, especially at higher potentials. These results indicate that the oxidized and reduced forms of these films are structurally and/or compositionally different.

Efforts were made to determine the apparent diffusion coefficients, *D*_{app}, from the *i/t* data. For the reduction reaction (overlap of film oxidation with OER made oxidation kinetics difficult to establish), *D*_{app} was found to be in the range of 10⁻⁹ to 10⁻¹¹ cm²/s. In this calculation, the film thickness, measured *in situ* by ellipsometry and *ex situ* by SEM methods, was assumed to be the same in the oxidized and reduced states. The *D*_{app} values were higher for the 50:50 Ni-Co vs. the Ni oxide films, indicating that the addition of Co to Ni oxide leads to a notable kinetic advantage. The SG film formation conditions, especially the drying temperature and time, strongly influence their thickness, crystallite size, and also the dimensions of the channels between SG oxide nanocrystals. This, in turn, strongly affects the *D*_{app} values of the mobile species (Na⁺ and OH⁻) involved in the redox reaction, e.g., higher drying temperatures appear to shrink the film, compressing the channel size and decreasing the *D*_{app} values.

Ac impedance experiments were also conducted, yielding very high double layer capacitances, indicative of high surface area films, and a good measurement was obtained of the charge storage capacity of these films from the low frequency capacitance. Also, *D*_{app} values were calculated from the transition frequency in Nyquist plots; these were very close to those determined from the CV and *i/t* measurements.

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References

1. F.H. Moser and N.R. Lynam, US Patent 4,959,247 (1990).
2. I. Serebrennikova and V.I. Birss, *J. Electrochem. Soc.*, 147(10), 3614-3620 (2000).
3. I. Serebrennikova and V.I. Birss, *J. Electroanal. Chem.*, 493, 108-116 (2000).