

The Intercalation of Lithium in Nickel Oxide and Its Electrochromic Properties

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ABSTRACT

Under rigorously dry conditions, nickel oxide sputtered samples undergo a reversible lithium intercalation-deintercalation process which is accompanied by a net electrochromic effect. The characteristics of the process have been studied by cyclic voltammetry and by optical transmittance. The use of lithium-intercalated nickel oxide as a new type of counter-electrode in electrochromic windows is also discussed.

Nickel oxide is a well-studied material due to its use in positive electrodes in batteries (1-3). More recently, research on the optical properties of hydrated nickel oxide has also been of considerable interest, due to its potential use as an inorganic anodic ion-insertion electrochromic material (4, 5). So far it has been assumed that nickel oxide colors anodically only in its hydrated form in aqueous electrolytes. Accordingly, most of the research on the electrochemical and electrochromic properties of this oxide has been conducted in aqueous media (6, 7). In fact, the general thinking is that water has a key role in the electrochromic mechanism. The exact nature of this mechanism, however, is an object of controversy. Some authors describe the process as a double extraction of protons and electrons (4) and others as a double injection and extraction of oxydriles and electrons (8). In a way, this controversy is similar to that related to the mechanism of electrochemical/electrochromic reaction of iridium oxide (9).

In this paper, we show that nickel oxide sputtered samples, if kept in rigorously dry conditions, can undergo a reversible lithium intercalation-deintercalation process, which is accompanied by a net electrochromic effect. This has been proved by electrochemical (cyclic voltammetry) and optical (transmittance spectra) measurements.

Experimental

Nickel oxide samples and tungsten oxide samples, sputtered on indium-tin-oxide (ITO)-coated glasses, were kindly provided by Dr. G. C. Granqvist of the Chalmers Institute of Technology, in Sweden. Details on the preparation may be found in Ref. (10). The nickel oxide samples, of average thickness of 600Å, were dc-sputtered on indium-tin-oxide (ITO)-coated glasses of 1 cm² surface. Analyses of samples indicated a NiO_z stoichiometry, with 1 < z < 1.66. The tungsten oxide—WO₃—samples, of average thickness of 3000Å, were obtained by RF sputtering onto ITO-coated glasses of 1 cm² surface.

Propylene carbonate and lithium perchlorate, both reagent grade products, were further purified by distillation and by melting under vacuum, respectively. The electrochromic properties of nickel oxide samples (and of tungsten oxide samples) were brought out using three-electrode cells with lithium strips as reference and counterelectrodes and a 0.1M solution of lithium perchlorate in propylene carbonate (here briefly indicated as LiClO₄-PC) as electrolyte. The cells were assembled and maintained in a controlled-atmosphere dry box (water content less than 10 ppm).

The characteristics of the electrochromic processes were investigated by cyclic voltammetry, using in-house-developed, computer-controlled equipment. The electrochromic activation of nickel oxide samples was performed by promoting lithium intercalation via cathodic polarization at very low current density (typically 5 μm cm⁻²). The

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electrochromic windows were realized by facing an activated pre-lithiated nickel oxide ITO-coated glass electrode with a pristine tungsten oxide ITO-coated glass electrode in the LiClO₄-PC electrolyte. Also, these two-electrode windows were assembled and kept in the dry box. The performances were tested by cyclic voltammetry and by optical transmittance, detected *in situ* directly into the dry box. For this purpose, the window was placed on an in-house-developed optical bench having a He-Ne laser (6328Å) source and a UDD light detector. All the values of transmittance quoted in this work are relative to the system (cell + electrolyte + samples), considering 100% transmittance the value associated with the system (cell + electrolyte).

Results and Discussion

Figure 1 illustrates the cyclic voltammetric curves of an as-deposited nickel oxide sample in the LiClO₄-PC electrolyte. The first cycle presents a cathodic current that becomes significant below 2.5V; however, when the cycle is reversed at 1.2V, no net anodic current is observed, thus showing that the cathodic process is not reversible. On continuous cycling, maintaining the cathodic limit, E_c, fixed at 1.2V, the cathodic current decreases significantly and finally almost vanishes (see cycle 2).

However, if E_c is moved to more negative values, two new cathodic peaks, indicated as c₁ and c₂ in Fig. 1, show up. Two peaks, labeled as a₁ and a₂, also appear in the following anodic scan and the overall voltammetric behavior is repetitive over a large number of cycles (see cycle n in

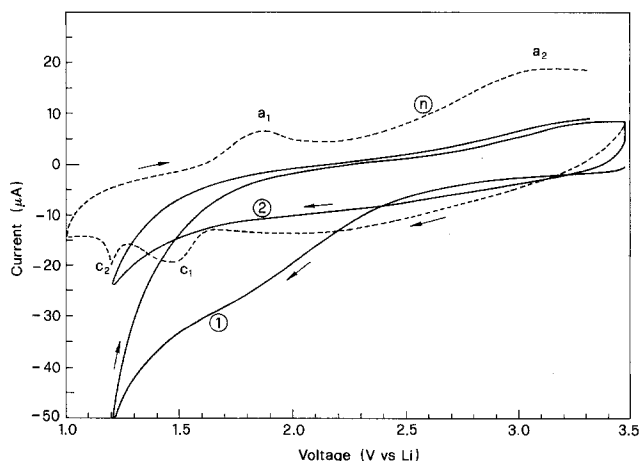


Fig. 1. Cyclic voltammetry of a sputtered nickel oxide sample in the LiClO₄-PC electrolyte at room temperature. Cycles 1 and 2 are the first and second cycles obtained with a fixed cathodic limit of 1.2V. Cycle n represents the repetitive behavior at more negative voltage limits. Scan rate: 10 mV s⁻¹. Lithium reference and lithium counter.

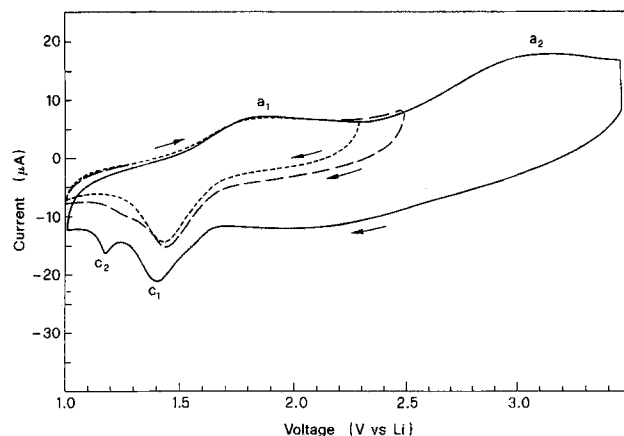


Fig. 2. Cyclic voltammogram of the sputtered nickel oxide sample in the $\text{LiClO}_4\text{-PC}$ electrolyte at room temperature and with different anodic voltage limits. Scan rate: 10 mV s^{-1} . Lithium reference and lithium counter.

Fig. 1, where typically $n = 50$). If now the voltammogram is reversed at a more negative anodic limit, the cathodic peak c_2 tends to disappear (Fig. 2), thus making it clear that peaks a_1/c_1 and a_2/c_2 are related. The described behavior is reproducible and may only slightly vary (in terms of peak position and height) from sample to sample, depending upon preparation history. In any case, reproducibility and efficient results critically require operations in rigorously dry conditions, and the use of non-stoichiometric NiO_x samples.

The interpretation of the voltammetric curves is not simple. As a tentative explanation, one may assume that the first cycles at E_c fixed to 1.2V are accompanied by an initial and irreversible intercalation of lithium (large cathodic peak of cycle 1 in Fig. 1), which may induce a phase modification of the original nickel oxide sample. Indeed, modification of phases during cyclic voltammogram of hydrated nickel oxide has been reported by various authors (4, 8). Obviously, in the present case, further studies, possibly by spectroscopic and/or x-ray analyses, are needed to confirm

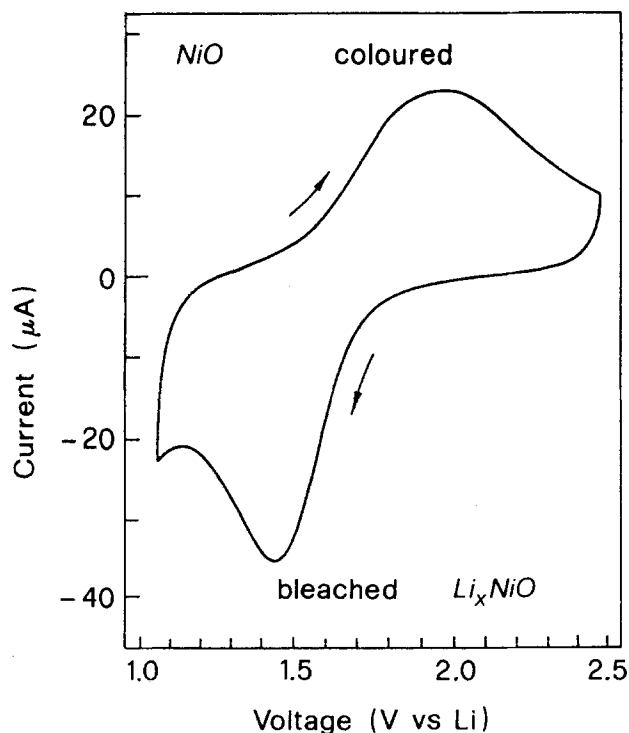


Fig. 3. Cyclic voltammogram of an 'electrochemically activated' nickel oxide sputtered sample in the $\text{LiClO}_4\text{-PC}$ electrolyte at room temperature. Scan rate: 10 mV s^{-1} . Lithium reference and lithium counter.

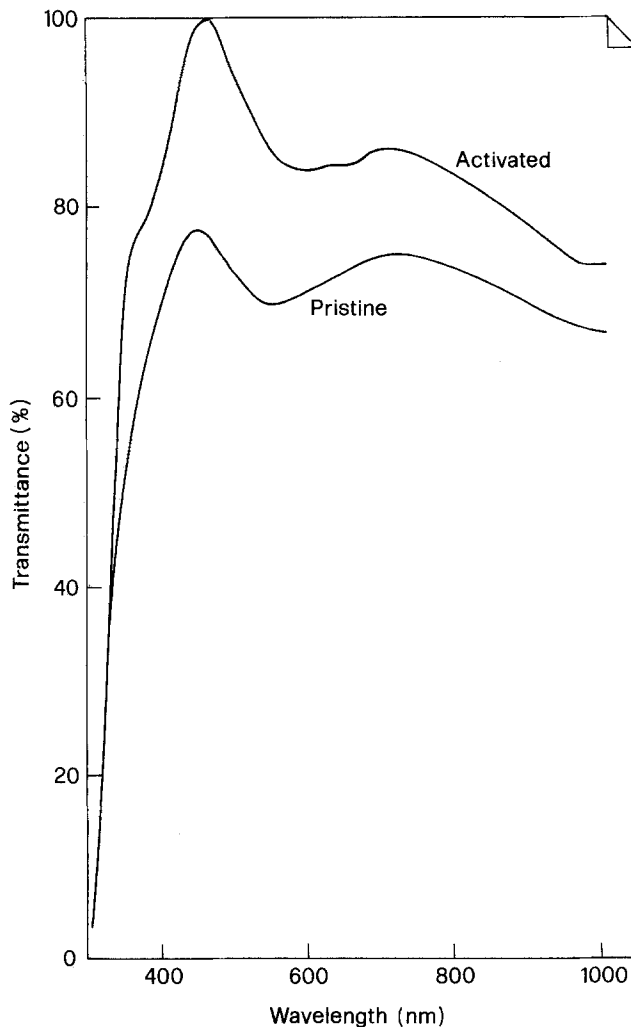


Fig. 4. Optical transmittance of pristine and 'activated' nickel oxide samples.

the hypothesis of a new structure following the initial insertion of lithium in nickel oxide.

On the other hand, in this preliminary work it is important to point out that a large current which can be attributed to lithium electrodeposition only develops when the first voltammetric cathodic scan is extended beyond 1.2V, and that only under this condition a corresponding anodic stripping peak shows up when the cycle is reversed. This confirms that the described initial irreversible voltammetric behavior obtained with E_c fixed at 1.2V cannot be due

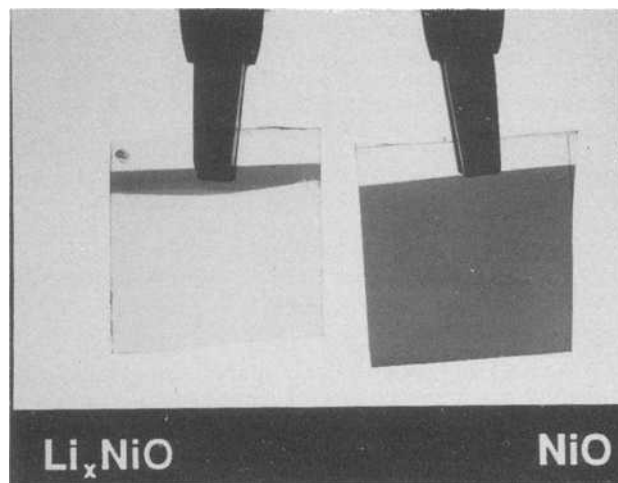


Fig. 5. Appearance of pristine (right side) and 'activated' nickel oxide samples.

