The interculation of Lithium in Nicker Oxide and its

Electrochromic Properties

S. Passerini and B. Scrosati*

Dipartimento di Chimica, Università di Roma 'La Sapienza,' Rome, Italy

A. Gorenstein

Instituto de Fisica — UNICAMP, Campinas S. P., Brasil

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 counterelectrode 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 NiO₂ 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 0.1*M* 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-housedeveloped, 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 μ m cm⁻²). The

* Electrochemical Society Active Member.

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 inhouse-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 c_1 and c_2 in Fig. 1, show up. Two peaks, labeled as a_1 and a_2 , 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.

J. Electrochem. Soc., Vol. 137, No. 10, October 1990 © The Electrochemical Society, Inc.

Downloaded on 2014-11-25 to IP 143.106.108.94 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Fig. 2. Cyclic voltammetry of the sputtered nickel oxide sample in the LiClO₄-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 voltammetry 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_z 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 voltammetry 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 LiClO₄-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.



Fig. 6. Galvanostatic activation of a nickel oxide (ITO-glass) sample in the LiClO₄-PC electrolyte. Current density: $5 \ \mu A \ cm^{-2}$.

to an electrodeposition but rather must be due to a different process, which might be the above assumed lithium intercalation reaction. Taking this assumption as realistic, it is reasonable to consider that the initial inserted lithium may 'activate' the electrode by somewhat widening the nickel oxide structure, favoring further and reversible lithium intercalation. Under such a modified condition, this intercalation process would be rapidly repetitive and could be possibly revealed by peak c_1 (lithium intercalation) and peak a_1 (lithium deintercalation) of Fig. 2.

To confirm this, the response of an electrochemically 'activated' nickel oxide sample was controlled again by cyclic voltammetry, maintaining the voltage range between the a_1 - c_1 peak limits. The voltammogram shows a well-defined and repetitive behavior, with which a net electrochromic effect is associated (Fig. 3). This is further confirmed by Fig. 4, which compares the optical transmittance of pristine and activated nickel oxide samples, and by Fig. 5, which shows the appearance of the two samples. The electrode becomes colored (brown) during the anodic scans and returns to bleached during the cathodic scans, with a contrast which remains reproducible for a large number of cycles.



Fig. 7. Cyclic voltammetry of sputtered tungsten oxide (ITO-glass) sample in the LiClO₄-PC electrolyte at room temperature. Scan rate: 10 mV s⁻¹. Lithium reference and lithium counter.

In conclusion, one may associate the described effects with the following oversimplified electrochemical process

$$\begin{array}{cc} xLi^{+} + Li_{y}NiO_{z} + xe^{-} \iff Li_{(x+y)}Ni_{x}O_{z} \\ (colored) & (bleached) \end{array}$$
[1]

where $\operatorname{Li}_{y}\operatorname{NiO}_{z}$ indicates the 'activated' nickel oxide and $\operatorname{Li}_{(x+y)}\operatorname{NiO}_{z}$ the Li-intercalated nickel oxide. The above described results show that activated nickel oxide electrodes show a fast and reversible electrochromic behavior which is associated with intercalation of lithium. The lithium intercalation process may be promoted by cyclic voltammetry or, more extensively, by cathodically polarizing the nickel oxide electrode in the LiClO₄-PC non-aqueous electrolyte. The cathodic polarization should preferably be run at low current density (typically 5 μ m cm⁻²) to favor the diffusion of lithium throughout the electrode.

Figure 6 illustrates a typical result of such a galvanostatic activation of a nickel oxide sample, reported in terms of acquired transmittance *vs.* time of polarization. The transmittance progressively increases upon current flow (and thus upon lithium intercalation) to approach a 100% value. Interestingly, activated nickel oxide electrodes may intercalate a consistent amount of lithium still



Fig. 8. Cyclic voltammetry (lower part, WO_3 working electrode) of the Li_xNi_yO_x/WO₃ electrochromic window. Sweep rate: 10 mV s⁻¹. Lithium reference. In the upper part of the figure is shown the optical transmittance of the entire device together with the separate transmittance of the two electrodes.

Downloaded on 2014-11-25 to IP 143.106.108.94 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).





retaining the bleached condition. Therefore, under this situation, nickel oxide can exchange lithium without losing full transparency, and thus behave as an optically passive, lithium sink electrode.

These properties make activated nickel oxide of consistent interest for the realization of new types of efficient electrochromic windows. An electrochromic window is basically a device capable of passing from a fully colored to a fully transparent state. Lately, there has been a renewed interest in electrochromic windows, due to their importance for energy control in buldings and cars (11, 12). Most commonly, these windows use tungsten oxide for the main electrochromic electrode. Effectively, tungsten oxide shows in the cited LiClO₄-PC electrolyte a very reversible electrochromic behavior (Fig. 7), related to the following lithium intercalation-deintercalation process

$$\begin{array}{ccc} \mathrm{xLi}^{+} + \mathrm{WO}_3 + \mathrm{xe}^{-} & \longleftrightarrow & \mathrm{Li}_x \mathrm{WO}_3 \\ \mathrm{(bleached)} & \mathrm{(colored)} \end{array}$$

However, the use of WO3 as the primary electrode in an electrochromic window requires a counterelectrode which is either optically passive or electrochromic in a complementary mode. On the basis of the results here presented, Li-activated nickel oxide appears to fulfill well, the conditions of an efficient complementary counterelectrode. To control this assumption, we have assembled the window

$$Li_{(x+y)}NiO_z/LiClO_4-PC/WO_3$$
 [3]

formed by facing a Li-activated nickel oxide electrode to a tungsten oxide electrode (both on ITO-coated glass supports) in the LiClO₄-PC electrolyte. The nickel oxide electrode was preactivated by galvanostatic intercalation in a separate cell. The window shows a net and reversible electrochromic behavior, as revealed by Fig. 8, which illustrates the cyclic voltammetry (WO3 working electrode and $Li_{(x+y)}NiO_z$ counterelectrode) and the *in situ* optical transmittances of the entire device, as well as of two single electrodes.

During the cathodic scan, the window is dark and the transmittance decays, while in the following anodic scan the window becomes clear and the transmittance rises, and this behavior, reproducible for many cycles, may be related to the following electrochromic process

$$\begin{array}{ccc} \operatorname{Li}_{(x+y)}\operatorname{NiO}_{z} + \operatorname{WO}_{3} &\longleftrightarrow & \operatorname{Li}_{y}\operatorname{NiO}_{z} + \operatorname{Li}_{x}\operatorname{WO}_{3} & \quad [4] \\ (\text{clear}) & (\text{dark}) \end{array}$$

which involves the passage of lithium from one electrode to the other, in a sort of 'rocking-chair' configuration mode, which has been proved to be very efficient and convenient for other types of electrochemical devices (13). In the case of the window under study, the charge transferred amounts to about 20 mC cm⁻², and during the switching the voltage of the nickel oxide counterelectrode varies

from 1.0V to 4.5V vs. Li. These conditions led us to suppose that peaks a_2 and c_2 (see Fig. 1) may also be involved in the overall electrochromic process.

The results of Fig. 8 indicate that by configurations similar to [3], new and efficient types of WO₃-based electrochromic windows may be developed. Indeed, the window has an efficient, reproducible behavior, since the optical properties remain unchanged for many cycles (Fig. 9). Due to the importance and to the basic interest in the processes here described, further investigation on the electrochromism of nickel oxide in lithium non-aqueous electrolytes, and on the design and performance of related displays, is presently in progress in our laboratories.

Acknowledgments

The authors wish to thank Dr. G. C. Granqvist and his group in Sweden for providing the sputtered samples. One of us (A.G.) is grateful to the International Center of Theoretical Physics (ICTP) of Trieste for a Visiting Scientist Fellowship. Finally, the financial support of Ministero Pubblica Istruzione (MPI, 40%) is acknowledged.

Manuscript submitted Sept. 26, 1989; revised manuscript received May 20, 1990.

The University of Rome assisted in meeting the publication costs of this article.

REFERENCES

- 1. G. W. Briggs, E. Jones, and W. F. K. Winne-Jones, Trans. Faraday Soc., 51, 1433 (1955).
- 2. R. Barnard, C. F. Randell, and F. L. Tye, J. Appl. Electrochem., 10, 109 (1980).
- 3. C. A. Vincent, F. Bonino, M. Lazzari, and B. Scrosati, 'Modern Batteries," Arnold Pu, London (1987)
- 4. J. S. E. M. Svensson and G. C. Granqvist, Appl. Phys. Lett., 49, (23) 1566 (1986).
- 5. W. Estrada, A. M. Andersson, and C. G. Granqvist, J. Appl. Phys., 64, 3678 (1988).
- 6. M. Fantini and A. Gorenstein, Solar Energy Mat., 16, 487 (1987)
- 7. A. Gorenstein, F. Decker, W. Estrada, C. Esteves, A. Andersson, S. Passerini, S. Pantaloni, and B. Scrosati, J. Electroanal. Chem., 277, 277 (1990). 8. F. Hahn, D. Floner, B. Beden, and C. Lamy, Electro-
- chim. Acta, 32, 1631 (1987). 9. G. Gottesfield, J. D. E. McIntyre, G. Beni, and J. L. Shay, Appl. Phys. Lett., 33, 208 (1978).
- 10. T. Eriksson and G. C. Granqvist, J. Appl. Phys., 60, 2081 (1986).
- 11. J. S. E. M. Svensson and G. C. Granqvist, Solar Energy Mat., 11, 29 (1984).
- 12. R. D. Rauh and S. F. Cogan, Solid State Ionics, 28-30, 1707 (1988).
- B. Di Pietro, M. Patriarca, and B. Scrosati, J. Power Sources, 8, 289 (1982).