Title
Sol-Gel Deposited Electrochromic Coatings

Author
Ozer, N.

Publication Date
1995-06-01

CONF-9506412--1

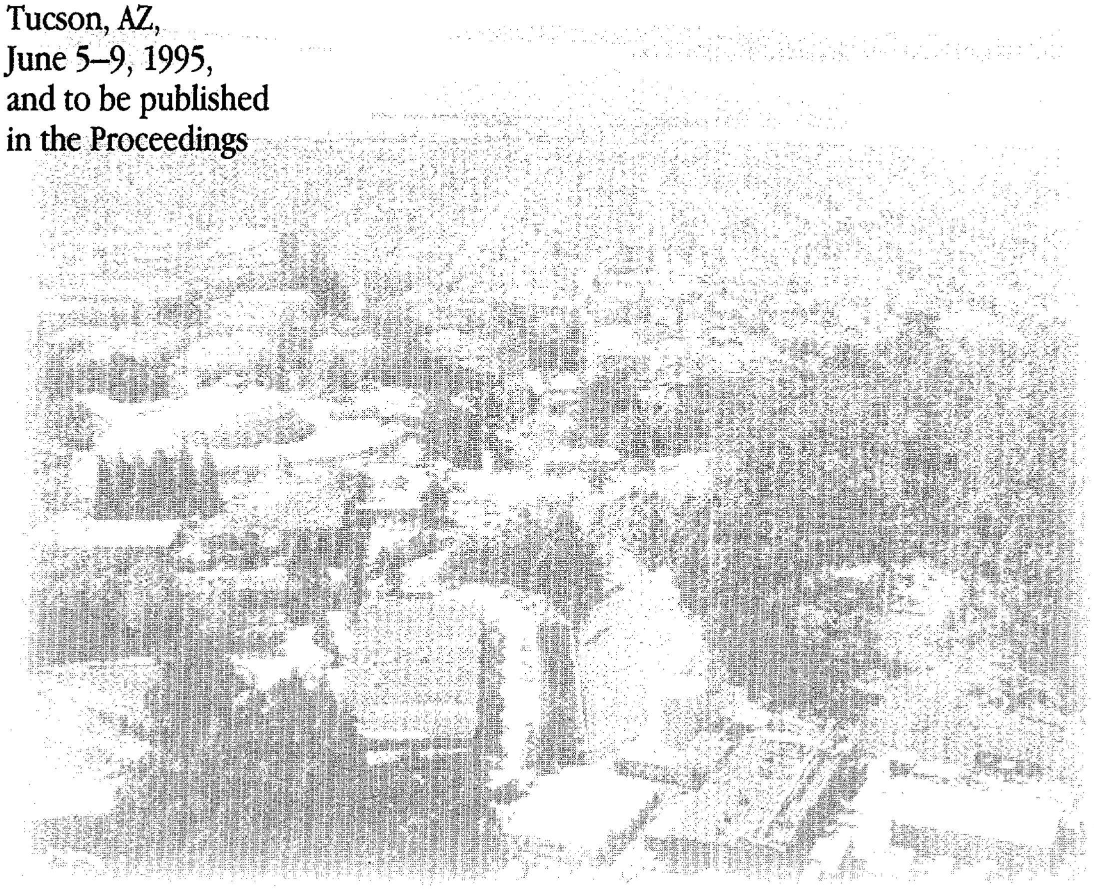
LBL-38527
UC-1600

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Sol-Gel Deposited Electrochromic Coatings

Nilgun Ozer and Carl M. Lampert
Energy and Environment Division

June 1995
Presented at the
Optical Interference Coatings Topical Meeting,
Tucson, AZ,
June 5–9, 1995,
and to be published
in the Proceedings



DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

This report has been reproduced directly from the best available copy.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

LBL-38527
UC-1600

Sol-Gel Deposited Electrochromic Coatings

Nilgun Ozer and Carl M. Lampert

Energy and Environment Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

June 1995

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Sol-gel Deposited Electrochromic Coatings

Nilgun Ozer and Carl M. Lampert

Lawrence Berkeley Laboratory,
University of California, M.S.62-203,
Energy and Environment Div., Berkeley, CA 94720
USA Tele: 510-486-6093, Fax: 510-486-7339

ABSTRACT

Electrochromic devices have increasing application in display devices, switchable mirrors and smart windows. A variety of vacuum deposition technologies have been used to make electrochromic devices. The sol-gel process offers an alternative approach to the synthesis of optical quality and low cost electrochromic device layers. This study summarizes the developments in sol-gel deposited electrochromic films. The sol-gel process involves the formation of oxide networks upon hydrolysis-condensation of alkoxide precursors. In this study we cover the sol-gel deposited oxides of WO_3, V_2O_5, TiO_2, Nb_2O_5, and NiO_x.

1. INTRODUCTION

The electrochromic properties of transition metal oxides have been extensively studied during last decade for potential use in display devices or smart windows [1-2]. Electrochromism is a reversible color change in a material induced by injected/ejected electrical charge and ions. The electrochromic material has to be deposited as a thin layer onto transparent electrode. This is usually done by vacuum evaporation [3], sputtering [4] or electrolytic deposition [5]. The sol-gel process offers a new approach to the synthesis of oxide coatings [6]. In sol-gel process molecular precursors are transformed into an oxide network via organic polymerization reactions. The molecular precursor is usually a metal alkoxide $M(OR)_n$, and polymerization occurs via hydrolysis and condensation [7]. The overall reaction can be described as follows:

Hydrolysis : $M(OR)_n + nH_2O \rightarrow M(OH)_n + n\,ROH$

Condensation : $M(OH)_n \rightarrow MO_{0.5n} + (0.5n)\,H_2O$.

Sol-gel derived electrochromic metal oxides can be made from colloidal solutions by dipping, spin coating or spying [1]. They are easy to synthesize and exhibit a rather good electrochromic behavior [6,8-10]. This paper reports a discussion about the electrochromic properties of WO_3, TiO_2, Nb_2O_5, V_2O_5 and NiO_x layers. It is based on published data from literature together with results from our laboratory.

2. RESULTS AND DISCUSSION

2.1. Tungsten Oxide

Tungsten oxide coatings have been deposited from a number of sol-gel precursors such as tungstic acid solutions [8,11], tungsten alkoxides based solutions [12], and chloro-alkoxide [13]. Films prepared from choloro-alkoxide showed better uniformity than those prepared from colloidal route. Sol-gel deposited tungsten oxide shows a transparent to dark blue electrochromism with ion injection. A proposed reaction for coloration is based on a dual mechanism a) ion insertion to the film; b) electron insertion. The reaction can be interpreted as :

$$\underset{\text{transparent}}{WO_3 + x\,A^+ + x\,e^-} \Longleftrightarrow \underset{\text{blue}}{A_xWO_3}, \ (A^+ = H^+ \text{ or } Li^+)$$

Fig. 1 shows a typical cyclic voltammogram of sol-gel spin coated (SG) WO_3 films prepared from tungsten dichloride triethoxide compared with the ones prepared by vacuum techniques.

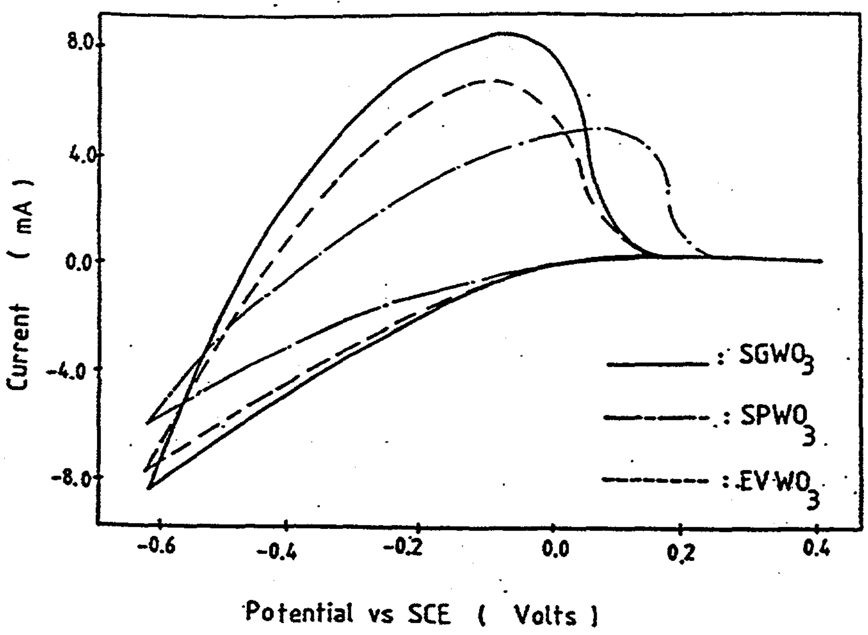


Fig. 1 . Cyclic voltammograms of WO_3 films. 0.1 H_2SO_4 solution was used as an electrolyte with a sweep rate of 20mV/s. The film thicknesses were about 200 nm for each film. The films color under a negative potential.

2.2. Titanium Oxide

Sol-gel titanium oxide films can be formed from the classical alkoxy route and by the colloidal route [6,9,14]. They appear to be amorphous by X-ray diffraction. Upon heating the films crystallized into TiO_2 anatase around 400 °C. Amorphous TiO_2 undergoes an electrochromic reactions according to :

$TiO_2 + x\,Li^+ + xe^- \Longleftrightarrow Li_xTiO_2$ or $TiO_2 + H^+ + e^- \Longleftrightarrow TiOOH$
transparent gray transparent blue

Titanium oxide also colors when reduced by ion insertion, but its coloration efficiency is lower than tungsten oxide. Amorphous films change from transparent to gray or blue when reduced by Li^+ or H^+ ions.

2.2. Niobium and Vanadium Oxides

The group V-B oxides, namely Nb_2O_5 and V_2O_5 exhibit cathodic electrochromism like WO_3. Although the change in optical spectrum between oxidized and reduced state by ion intercalation is not as large WO_3, it has been shown that these oxides have good Li^+ ion storage capability and reversibility [2,6,15]. The reversibility of V_2O_5 in the crystalline state is superior to that in the amorphous state. Sol-gel niobium and vanadium oxide films have been synthesized from alkoxides, oxoalkoxides or alkoxyhalides based solutions [15-17]. XPS and optical spectra of the colored V_2O_5 and Nb_2O_5 coatings together with electrochemical experiments show that the electrochromic properties can be described by:

$Nb_2O_5 + x\,Li^+ + x\,e^- \Longleftrightarrow Li_x\,Nb_2O_5$ or $Nb_2O_5 + 2\,H^+ + 2\,e^- \Longleftrightarrow Nb_2O_3(OH)_2$
transparent brown transparent green-blue

$V_2O_5 + x\,Li^+ + x\,e^- \Longleftrightarrow Li_x\,V_2O_5$
transparent yellow gray

2.4. Nickel Oxide

Nickel oxide is presently the subject of several studies [2,17]. Nickel oxide films have been formed by dissolving or reacting nickel nitrates in alcohol and then using the product as precursors [18]. The coloration mechanism has been determined for protons by J. C. Giron [19].

The reaction involves two coupled reactions:

$Ni(OH)_2 \Longleftrightarrow NiOOH + H^+ + e^-$ and $H^+_{film} + OH^-_{electrolyte} \Longleftrightarrow H_2O_{film}$
transparent brown

Sol-gel films made from nickel methoxyethoxide precursor also showed a transparent to brown electrochromism with Li^+ insertion. These films colored by anodic transfer of electrons out of the film couple with anion injection from the electrolyte.

Table 1. summarizes some properties of the sol-gel deposited electrochromic layers.

Table 1. Sol-gel electrochromic coatings

Material	Color neutral	oxidized or reduced form	Stability (lifetime)	Electrode	Reference
WO_3 (C)	Transparent	Blue	10^4 cycles	$LiClO_4$	11-13
TiO_2 (C)	Transparent	Gray or blue	10^3 cycles	$LiClO_4$	6, 14
Nb_2O_5 (C)	Transparent	Brown, gray	10^4 cycles	$LiClO_4$	1, 15
V_2O_5 (A)	Light yellow	Brown,green	10^3 cycles	$LiClO_4$	1, 6
NiO_x (A)	Light green	Brown	10^3 cycles	$LiClO_4$	present work

note: (C) cathodically coloring, (A) anodically coloring.

2.5. Sol-gel made devices

The construction of display devices or smart windows consist of typically a (1) transparent conductor (ITO), (2) electrochromic layer, (3) solid electrolyte or ion conductor, (4) ion storage layer, (5) transparent conductor. Recently, the sol-gel process has been also adopted to prepare a variety of inorganic type solid electrolytes [20, 21]. An all sol-gel electrochromic device has been realized using sol-gel coatings with the configuration glass /ITO /WO_3 /TiO_2 /TiO_2-CeO_2 /ITO /glass [22]. The optical transmission spectra of these window is shown in fig. 2. This window has a fast optical response, but a short lifetime. Currently, several groups are trying to develop devices using some or all sol-gel deposited layers.

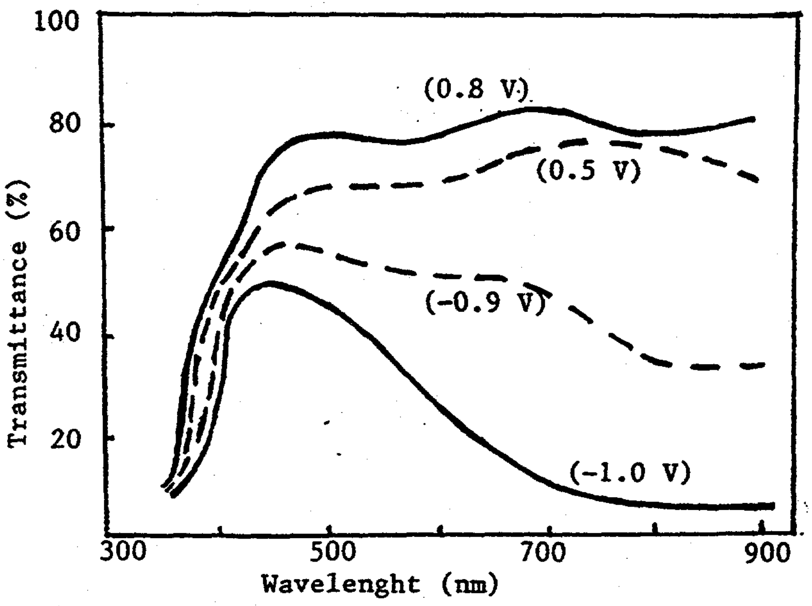


Fig. 2. Optical transmission of two electrochromic windows having the configuration : glass /ITO / H_xWO_3 / TiO_2-sg / CeO_2-TiO_2-sg / ITO / glass, where (——) is vacuum evaporated WO_3 and (----) is a sol-gel (sg) WO_3 .

4. SUMMARY

The sol-gel process offers new approaches for the fabrication of electrochromic materials. In the electrochromic device construction, microstructure control and chemical composition of the layers are important since they need to have electron and ion transport properties in addition to the optical requirements. Major advantages of the sol-gel process are ease of stoichiometry control and low sintering temperatures . Large-area coating can be easily deposited under ambient conditions by dip coating, spin coating, spying or even screen printing. Sol-gel deposited electrochromic layers have similar properties to those films deposited by vacuum techniques. We expect to see further developments in sol-gel deposited films for electrochromic devices in the future.

5. ACKNOWLEDGMENT

We wish to thank Dr. Phillip Baumeister for inviting this paper to the American Optical Society meeting. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

6. REFERENCES

1. C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam (1995).
2. C.M. Lampert, Solar Energy Mater., 11 (1984) 1.
3. Y. Fujita, K. Miyazaki, and C. Tatsuyama, Jpn. J. Appl. Phys., 24 (1985) 1082.
4. A. Deneuville. P. Gerard, and R. Billat, Thin Solid Films, 70 (1986) 203.
5. E. Andrukaitis, P.W.M. Jacobs, and J.W. Lorimer, Solid State Ionics, 27 (1988) 19.
6. M. Nabavi, S. Doeuff, C. Sanchez and J. Livage, Mater. Sci. Eng., B3 (1989)203.
7. J. Brinker, and G.W. Scherer, Sol-Gel Science, Academic Press, San Diego, 1990.
8. A. Chemseddine, R. Morineau and J. Livage, Solid State Ionics, 5 (1983) 357.
9. N. Ozer, Thin Solid Films, 214 (1992) 17.
10. A. Agrawal, J.P. Cronin and R. Zhang, Sol. Energy Mater. and Sol. Cells, 31(1993)9.
11. P. Judenstein, and J. Livage, SPIE Proc, 1328 (1990) 344.
12. H. Unuma, K. Tanooka, Y. Suzuki, T. Furasaki, K. Kodaira and T. Matsushita, J. Mater. Sci. Lett., 5 (1986) 1248.
13. A.M. Habib, and D. Glueck, Sol. Energy Mater., 18 (1989) 127.
14. N. Ozer, D.G. Chen, and J.H. Simmons, Ceramic Transactions ,V.20 (1991) 253.
15. N. Ozer , T. Barreto, T. Buyuklimanli, and C.M. Lampert, Sol. Energy Mater. and Sol. Cells, in press (1995).
16. C. Sanchez, M. Nabavi, and F. Taulelle, in Better Ceramics Through Chemistry III, MRS, Reno, April 1988, 121 (1988) 93.
17. F.H. Moser,and N.R. Lynam, U.S. Patent 4,855, 61 (1989).
18. F.H. Moser, and N.R. Lynam, U.S. Patent 4,959,247 (1990).
19. J.C. Giron and C.M. Lampert, The Electrochem. Soc. Extended Abst. V. 93-2 (1993) 652.
20. L.C. Klein, Solid State Ionics, 32-33 (1989) 639.
21. N. Ozer, Y.X. He, and C.M. Lampert, Proc. SPIE , 2255 (1994) 456.
22. M.A. Macedo, L.H. Dall'Antonia, and M.A. Aegerter, Proc. SPIE, 1758 (1992) 320.