

Inorganic Electrochromic Materials

Charles W. Hills

Literature Seminar

February 19, 1998

Electrochromic materials have garnered much attention for their optical properties.^{1,2,3,4} By definition, these materials change color upon electrochemical activation. This fact makes these materials of interest for use in such industrial applications as “smart windows” and “anti-dazzling” rearview mirrors. This group of materials includes transition metal oxides, hexacyano-metallates, viologens, conducting polymers, metal phthalocyanines, and metallopolymers.^{1,2}

The most widely studied of this group of materials are the transition metal oxides. Transition metal oxides fall into two categories, cathodic or anodic, depending on the mechanism for coloration.^{1,4,5} Cathodic species color upon the intercalation of cations (Li^+ , H^+ , Na^+ , K^+ , etc.); whereas, anodic species color upon deintercalation. A variety of chemical and physical methods can be employed to deposit these films, including evaporation, chemical vapor deposition, sputtering, sol-gel, and electrodeposition.^{1,4,6,7,8,9} The deposited films form layered or framework structures of MO_6 octahedra that include edge and corner sharing oxygens (Figure 1).⁵

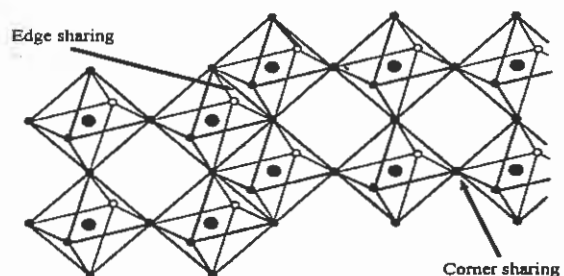


Figure 1

Within these films, a columnar microstructure is created. This allows for intercalation of ions, which balance the charge created by the insertion of electrons.¹ Tungsten oxide, the most studied material, is cathodic. The following reaction describes the electrochromic reaction:



Initially, tungsten oxide (WO_3) is “bleached,” or transparent, but upon electrochemical activation, the film (M_xWO_3) becomes “colored.” These states show interesting transmittance properties, with the “bleached” state having ~ 40-80% transmittance and the “colored” state ~ 10-30%.^{1,4,5,6(b)} This property, coupled with good cycling stability, has created interest in using these materials for variable transmittance and reflectance mirrors and windows.

Another group of materials gaining attention for their possible use in electrochromic displays, are the metal phthalocyanines. Monophthalocyanines complexes, typically nickel and copper, have been studied;¹⁰ however, lanthanide diphthalocyanines (Figure 2) have

attracted more interest due to better color contrast and color stability.^{11,12,13} There are several techniques for depositing these films, including electrodeposition and Langmuir-Blodgett (LB) technique. The Langmuir-Blodgett (LB) technique appears to provide the best qualities.¹⁴ LB films of phthalocyanines are well ordered, having long chains of phthalocyanine rings forming "columns."¹⁵

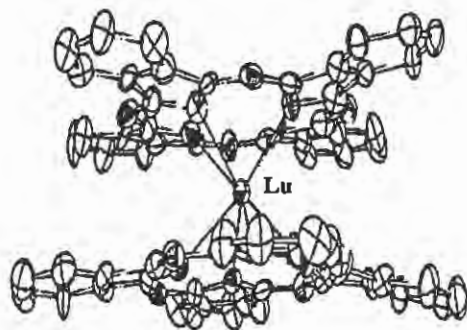


Figure 2A^{12(a)}

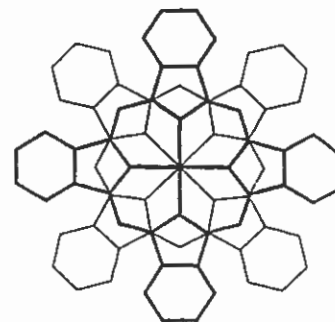


Figure 2B^{12(b)}

These compounds show distinct color changes. In a neutral state, these films are green, but can be changed to blue (reduction) and orange/red (oxidation) by applying an electrochemical potential. These films also provide good cycling stability, excellent contrast, and good stability.^{12(d),13} The combination of all these qualities make these LB films interesting for their use in display devices.

Though electrochromic materials are currently being used in some industrial applications, such as Gentex Corporations "Anti-dazzling mirrors,"² there is still room for growth. Most applications, such as "Smart Windows" and displays, are not yet economically viable. Further work is focusing on improving the stability of the electrochromic materials. Another push in the development of electrochromic devices (Figure 3)¹ is based on finding less

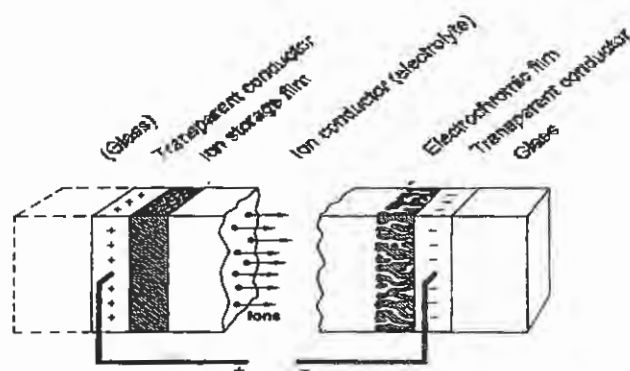


Figure 3

hazardous and more efficient electrolytes, as well as fine-tuning the interactions between the electrochromic film and the ion storage film.⁴

References

1. Granqvist, C.G., *Handbook of Inorganic Electrochromic Materials*, Elsevier: Amsterdam, 1995.
2. Green, M., "The Promise of Electrochromic Systems," *Chemistry and Industry* **1996**, 641.
3. Mortimer, Robert J., "Electrochromic Materials," *Chem. Soc. Rev.* **1997**, *26*, 147.
4. Granqvist, C. G.; Azens, A.; Hjelm, A.; Kullman, L.; Niklasson, G. A.; Ronnow, D.; Stromme Mattson, M.; Veszelei, M., "Recent Advances in Electrochromics for Smart Windows Applications." Original Manuscript.
5. Gellings, P. J.; Bouwmeester, H. J. M., *The CRC Handbook of Solid State Electrochemistry*, CRC Press: New York, 1997.
6. (a) Maruyama, T.; Arai, S., "Electrochromic Properties of Tungsten Trioxide Films Prepared by Chemical Vapor Deposition," *J. Electrochem. Soc.* **1994**, *141*, 1021. (b) Maruyama, T.; Kanagawa, T., "Electrochromic Properties of Tungsten Trioxide Thin Films Prepared by Photochemical Vapor Deposition," *J. Electrochem. Soc.* **1994**, *141*, 2435. (c) Henley, W. B.; Sacks, G. J., "Deposition of Electrochromic Tungsten Oxide Thin Films by Plasma-Enhanced Chemical Vapor Deposition," *J. Electrochem. Soc.* **1997**, *144*, 1045.
7. Morita, H.; Washida, H., "Electrochromism of Atmospheric Evaporated Tungsten Oxide Films (AETOF)," *Japanese Journal of Applied Physics* **1984**, *23*, 754.
8. Shen, P. K.; Chen, K. Y.; Tseung, A. C. C., "Electrochromism of Electrodeposited Tungsten Trioxide Films," *J. Electrochem. Soc.* **1994**, *141*, 1758.
9. Batchelor, R. A.; Burdis, M. S.; Siddle, J. R., "Electrochromism in Sputtered WO₃ Thin Films," *J. Electrochem. Soc.* **1996**, *143*, 1050.
10. (a) Li, H.; Guarr, T. F., "Formation of Electronically Conductive Thin Films of Metal Phthalocyanines via Electropolymerization," *J. Chem. Soc., Chem. Commun.* **1989**, 832. (b) Granito, C.; Goldenberg, L. M.; Bryce, M. R.; Monkman, A. P.; Troisi, L.; Pasimeni, L.; Petty, M. C., "Optical and Electrochemical Properties of Metallophthalocyanine Derivative Langmuir-Blodgett Films," *Langmuir*, **1996**, *12*, 472. (c) Chambrier, I.; Cook, M. J.; Cracknell, J.; McMurdo, J., "Synthesis and Characterisation of Some Substituted Mesogenic Phthalocyanines," *J. Mater. Chem.* **1993**, *3*(8), 841. (d) Cook, M. J.; McMurdo, J.; Miles, D. A.; Poynter, R. H.; Simmons, J. M.; Haslam, S. D.; Richardson, R. M.; Welford, K., "Monolayer Behaviour and Langmuir-Blodgett Film Properties of some Amphiphilic Phthalocyanines: Factors Influencing Molecular Organisation within the Film Assembly," *J. Mater. Chem.* **1994**, *4*(8), 1205. (e) Li, H.; Guarr, T. F., "Reversible Electrochromism in Polymeric Metal Phthalocyanine Thin Films," *J. Electroanal. Chem.* **1991**, *297*, 169.

11. (a) Souto, J.; Tomilova, L.; Aroca, R., "Spectroscopic Studies of Langmuir-Blodgett Monolayers of Praesodymium Bisphthalocyanines," *Langmuir*. **1992**, *8*, 942. (b) Rodriguez-Mendez, M. L.; Souto, J.; de Saja, J. A.; Aroca, R., "Electrochromic Display Based on Langmuir-Blodgett Films of Praesodymium Bisphthalocyanine," *J. Mater. Chem.* **1995**, *5*(4), 639.
12. (a) Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R., "Synthesis, Structure, and Spectroscopic Properties of the Reduced and Reduced Protonated Forms of Lutetium Diphthalocyanine," *Inorg. Chem.* **1988**, *27*, 1287. (b) Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R., "Synthesis, Structure, and Magnetic Properties of Lutetium(III) Phthalocyanine Derivatives: $\text{LuPc}_2 \cdot \text{CH}_2\text{Cl}_2$ and $[\text{LuPc}(\text{Oac})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$," *Inorg. Chem.* **1985**, *24*, 3162. (c) Moore, D. J.; Guarr, T. F., "Electrochromic Properties of Electrodeposited Lutetium Diphthalocyanine Thin Films," *J. Electroanal. Chem.* **1991**, *314*, 313. (d) Rodriguez-Mendez, M. L.; Aroca, R., "Electrochromic Properties of Langmuir-Blodgett Films of Bisphthalocyanine Complexes of Rare Earth Elements," *Chem. Mater.* **1992**, *4*, 1017. (e) Castaneda, F.; Plichon, V., "Electrochemistry of a Lutetium Diphthalocyanine Film in Contact with Acidic Aqueous Medium," *J. Electroanal. Chem.* **1987**, *233*, 77.
13. (a) Cook, M. J.; Daniel, M. F.; Harrison, K. J.; McKeown, N. B.; Thomson, A. J., "1,4,11,15,18-Hexa-alkyl-22,25-bis(carboxypropyl)phthalocyanines: Materials Designed for Deposition as Langmuir-Blodgett Films," *J. Chem. Soc., Chem. Commun.* **1987**, 1148. (b) Besbes, S. Plichon, V.; Simon, J.; Vaxiviere, J., "Electrochromism of Octaalkoxymethyl-Substituted Lutetium Diphthalocyanine," *J. Electroanal. Chem.* **1987**, *237*, 61. (c) Castaneda, F.; Piechocki, C.; Plichon, V.; Simon, J.; Vaxiviere, J., "Spectroscopic and Redox Properties of Alkyl-Substituted Lutetium Diphthalocyanines in Dichloromethane," *Electrochimica Acta* **1986**, *31*, 131. (d) Liu, Y.; Shigehara, K.; Hara, M.; Yamada, A., "Electrochemistry and Electrochromic Behaviour of Langmuir-Blodgett Films of Octakis-Substituted Rare-Earth Metal Diphthalocyanines," *J. Am. Chem. Soc.* **1991**, *113*, 440.
14. Gaines, George L., *Insoluble Monolayers at Liquid-Gas Interfaces*. Interscience Publishers: New York, 1966. (b) Goldenberg, Leonid M., "Electrochemical Properties of Langmuir-Blodgett Films," *J. Electroanal. Chem.* **1994**, *379*, 3.
15. Albouy, P. A., "Structure of Langmuir-Blodgett Films of Copper Phthalocyanine Derivatives," *J. Phys. Chem.* **1994**, *98*, 8543.