

OPTICAL MODELING OF A COMPLETE ELECTROCHROMIC DEVICE

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Abstract

Optical indices have been determined for thin films of all materials needed to model a typical electrochromic device. Two electrochromic materials, tungsten oxide and lithium nickel oxide, are widely used in electrochromic devices. The optical indices of the underlying transparent conductors as well as a polymer electrolyte were also analyzed. The optical data was obtained using a combination of variable-angle spectroscopic ellipsometry and spectroradiometry. The data was then fit to appropriate models of structure and dispersion in order to extract the optical indices of the materials. First, the optical indices of the transparent conductive substrates were obtained and fixed in the model. The best models correspond well to independent physical measurements of film structure, such as atomic-force microscopy and surface profiling. Surface roughness, gradient composition and other types of inhomogeneity are common in both the transparent conductors and electrochromic, resulting in particularly complex models. The polymer has a homogeneous structure, but obtaining optically smooth surfaces was a problem. Complete sets of data were produced over the entire solar spectrum for a range of colored states of the films. Using the data for each layer, a realistic electrochromic device was simulated.

Introduction

Calculation of the optical properties of a complex electrochromic device requires knowledge of the refractive index of each component layer. This data can then be used to predict spectral transmittance and reflectance at any angle of incidence. If the properties are also known as a function of charge density, then the intermediate states of the device can also be calculated. In turn, from these properties the energy performance can be calculated on an instantaneous or annual basis as well as visual performance parameters, such as color, color rendering, angular variations, privacy. Simulations of a realistic electrochromic office have even been produced in video format. Until recently, complete information of the optical indices of typical electrochromic materials has not been available.

To design a device with particular properties a systematic evaluation of different configurations is necessary. Important parameters in device design are individual layer thickness, different options for transparent and ion conductors, and the choice of

electrochromic layers. Practical considerations on material thickness will constrain the performance of devices. It is also possible, that measured optical indices will vary to an unacceptable degree over wide variations in thickness [1]. Another important consideration is to choose the thicknesses to maintain a match between the charge capacities of the electrode and counterelectrode [2]. Otherwise the device performance will be limited because one electrode will be prevented from achieving its full switching range.

Experimental

We previously determined the optical constants of a variety of materials used in electrochromic devices [1,3,4,5]. Optical measurements were performed over the entire solar spectrum, from 300 - 2500 nm, by a combination of variable-angle spectroscopic ellipsometry and spectroradiometry.

In this paper we calculate the optical properties of a typical electrochromic device based on a WO_3 electrode and a $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$ counter-electrode with ITO as transparent conductor and PEO as ion conductor as shown in Fig. 1. Results on different device configurations are also given.

ITO	1500 Å
$\text{Li}_{0.5+y}\text{Ni}_{0.5}\text{O}$	1250 Å
PEO	100 μm
Li_xWO_3	4000 Å
ITO	1500 Å
Glass substrate	1.24 mm

Fig. 1. Electrochromic device structure with typical thickness values

It was found empirically that $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$ can intercalate approximately 3.25 times more Li^+ ions per unit volume than WO_3 . This material is described in detail elsewhere [6].

The Polyethylene Oxide (PEO) ion conductor was cast onto a quartz substrate and measured in the way mentioned above. Since it is too thick to be conveniently measured by a light interference method, it was partly cut from the substrate to provide a sharp step for surface profilometry.

The extinction coefficient of the thick PEO layer is very small, which leads to many interference fringes in calculated transmittance and reflectance spectra. In a real device, however, interference fringes cannot be found, because the interfaces between the electrochromic layers and the polymer are never completely parallel over the width of the light beam. Other inhomogeneities in the ion conductor itself or interface roughness further diminish interference amplitudes.

In modeling devices with thinner ion conductors interference does not cause problems. To achieve a realistic model of an electrochromic device with a thick polymer ion conductor it is possible to virtually separate the device into halves giving up phase information at the boundary between electrochromic layer and ion conductor and thus intentionally excluding interference within the polymer [7].

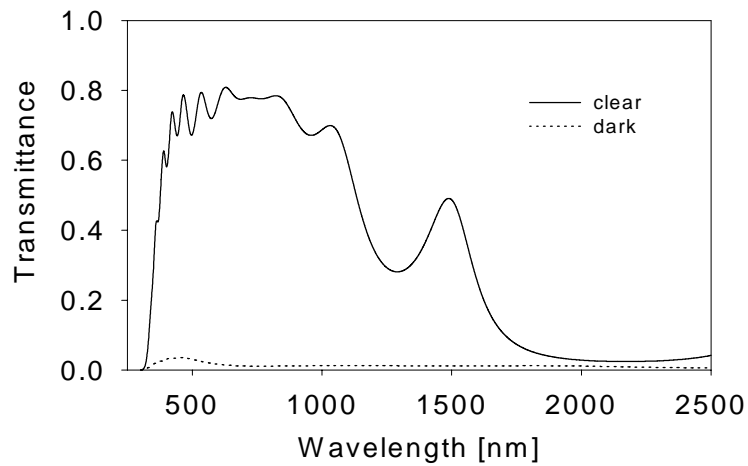


Fig. 2. Calculated normal transmittance in the clear and dark state of an electrochromic device

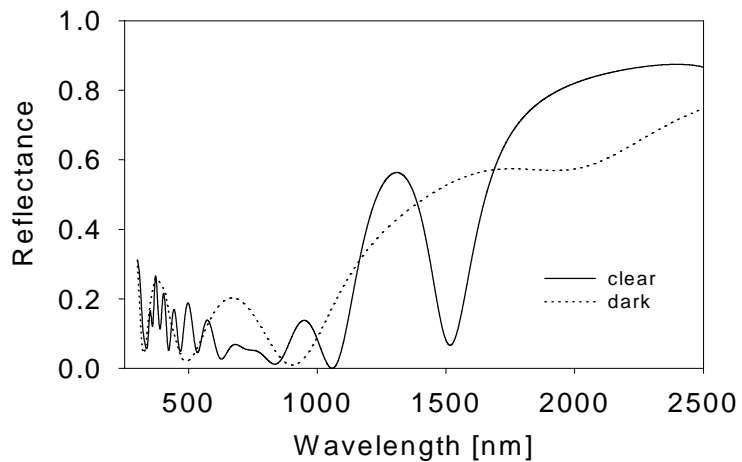


Fig. 3. Calculated normal reflectance in the clear and dark state from the $\text{Li}_{x+y}\text{Ni}_{1-x}\text{O}$ side

The transmittance and reflectance of a device calculated this way are shown in Fig. 2 and Fig. 3 for the clear and dark state. The theoretical switching range is from 75% to 2% visible transmittance for the device configuration shown in Fig. 1. The reflectance modulation is negligible as expected for amorphous WO_3 and $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$. The only difference is the dampened interference fringes in the dark state due to the increased absorption in the electrochromic layers. From the transmittance spectra it can be determined that the apparent color of such a device is dark gray in the colored state. The usual deep blue appearance of WO_3 -based devices is being neutralized by $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$, which is particularly absorbing in the lower part of the visible spectrum [6].

It is also necessary to calculate angle dependent radiometric properties in order to realistically calculate energy performance under solar radiation and coloration at different viewing angles.

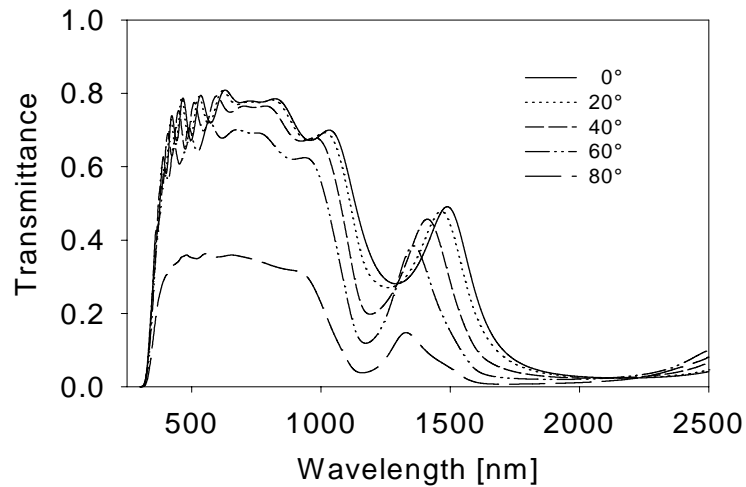


Fig. 4. Angular dependence of transmittance in the clear state

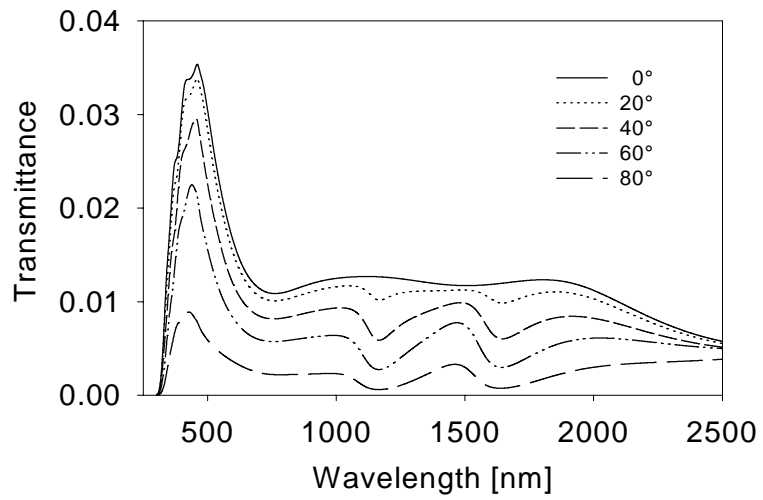


Fig. 5. Angular dependence of transmittance in the dark state

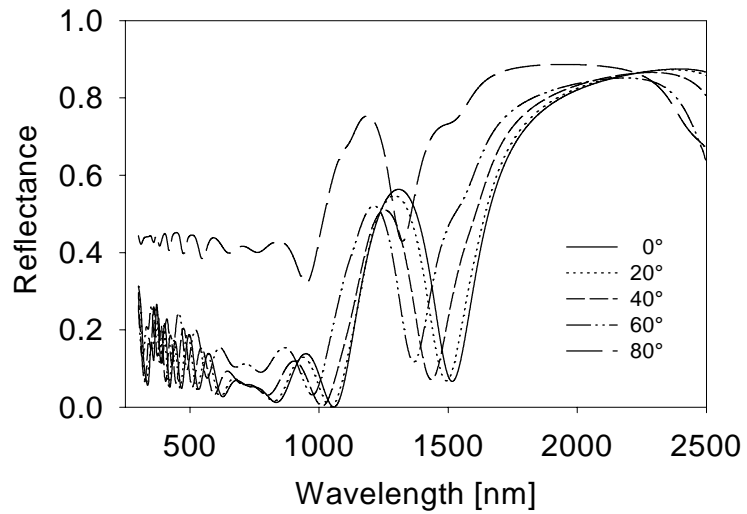


Fig. 6. Angular dependence of reflectance in the clear state from the $\text{Li}_{0.5+0.21}\text{Ni}_{0.5}\text{O}$ side

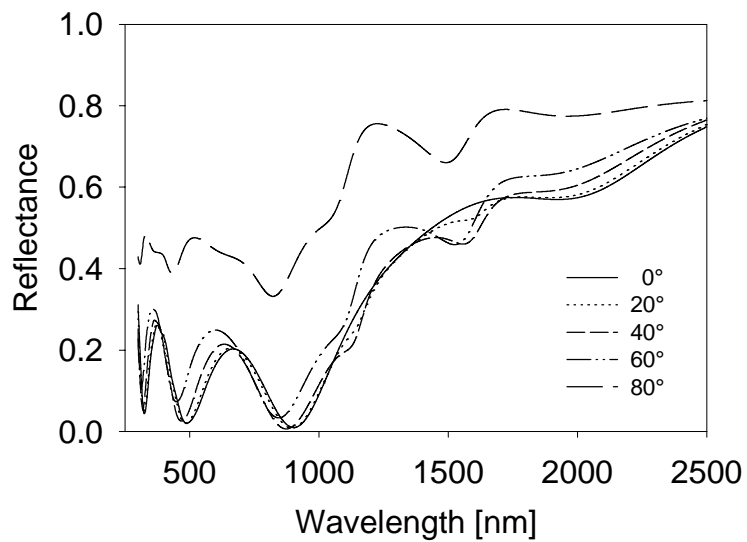


Fig. 7. Angular dependence of reflectance in the dark state from the $\text{Li}_{0.5+0.21}\text{Ni}_{0.5}\text{O}$ side

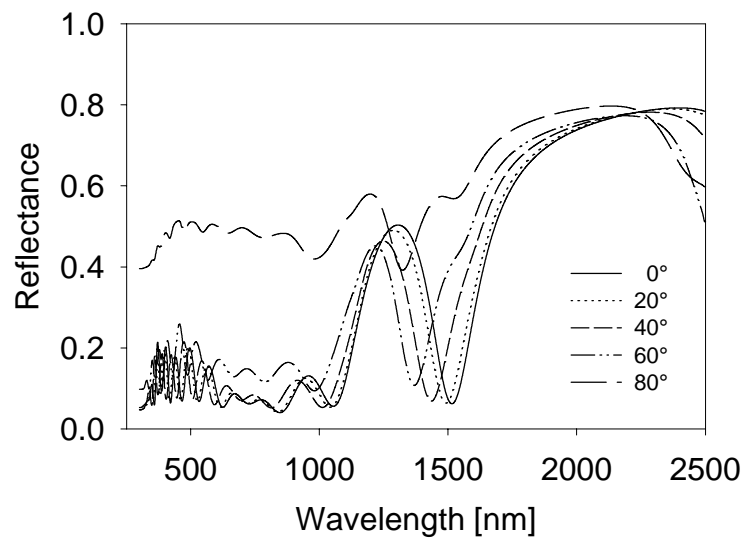


Fig. 8. Angular dependence of reflectance in the clear state from the $\text{Li}_{0.34}\text{WO}_3$ side

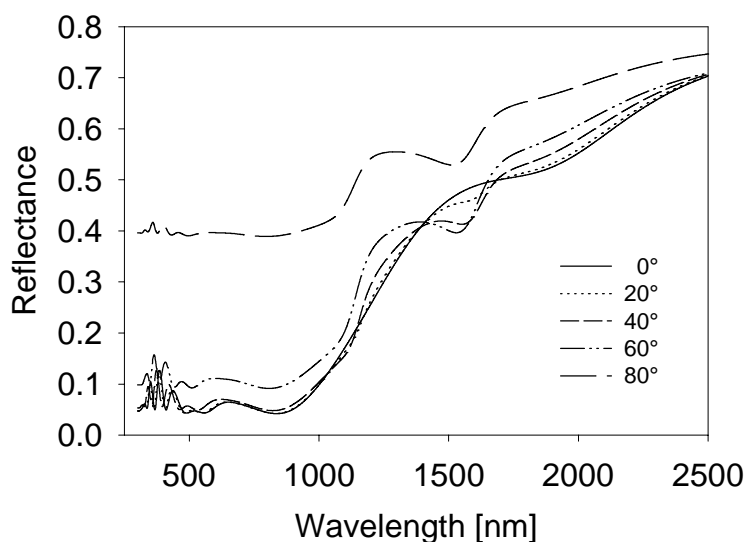


Fig. 9. Angular dependence of reflectance from the reverse side in the dark state from the $\text{Li}_{0.34}\text{WO}_3$ side in the dark state

Spectral transmittance and reflectance from the front ($\text{Li}_{x+y}\text{Ni}_{1-x}\text{O}$) and reverse (Li_zWO_3) side show only slight variations as a function of angles of incidence up to 60° , which does not produce a fundamental color change (Fig. 4 through Fig. 9).

A variety of different electrochromic device configurations were evaluated. Results on visible and solar transmittance in clear and colored states are given in table 1. The first configuration corresponds to the one treated above. In the second example the influence of the transparent conductor was evaluated by substituting the ITO against TEC15 glass, which is a multi-layer structure consisting mainly of $\text{SnO}_2:\text{F}$ [4]. The substitution of the more conductive ITO against the less expensive and chemically more stable $\text{SnO}_2:\text{F}$, however, leads to the loss of almost 5% visible transmittance.

electrode configuration	transparent conductor	T_{vis} [%]		T_{sol} [%]	
		clear	dark	clear	dark
400 nm WO_3 /125 nm $\text{Li}_x\text{Ni}_{1-x}\text{O}$	ITO	74.8	2.2	59.0	1.6
400 nm WO_3 /125 nm $\text{Li}_x\text{Ni}_{1-x}\text{O}$	TEC15	70.2	1.9	51.2	1.4
800 nm WO_3 /250 nm $\text{Li}_x\text{Ni}_{1-x}\text{O}$	ITO	67.9	0.1	56.7	0.1
400 nm WO_3 /100 nm LiCoO_2	ITO	55.7	7.0	46.6	4.6

Table 1. Calculated visible and solar transmittance values of different electrochromic device configurations

The third example shows, that if it were possible to build a device based on a WO_3 electrode and a $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$ counter-electrode of double thickness, almost total opacity ($T_{\text{vis}}=0.1\%$) in the dark state could theoretically be achieved. The fourth configuration uses LiCoO_2 as a different counter-electrode. LiCoO_2 is optically passive (5% modulation) and exhibits a large charge capacity.

Evaluation of more configurations are currently underway. It should be stressed that an optical model is valuable for device design, but calculated data cannot substitute for experimental data derived from the construction of a real electrochromic device. The benefit from previous modeling is that the large number of parameter permutations is reduced so that only the most promising electrochromic devices have to be assessed.

Conclusions

Angular dependent spectral transmittance and reflectance of an electrochromic device were calculated in the clear and dark state from 300 - 2500 nm. The switching range of a device based on a WO_3 electrode and a $\text{Li}_x\text{Ni}_{1-x}\text{O}$ counter-electrode was predicted to be from 75% to 2% visible transmittance and can be shifted by changing the thickness of the layers. The apparent color of such a device was determined to be a neutral gray from 0° to 80° viewing angle. Evaluating the influence of some of the parameters in the optical model demonstrated how knowledge of optical constants provides an important tool to systematically evaluate device design.

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References

- [1] K. von Rottkay, M. Rubin presented at the Int. Conference on Metallurgical Coatings and Thin Films (San Diego, USA, April 1996) and submitted to Thin Solid Films
 - [2] R.D. Rauh, S.F. Cogan, J. Electrochem. Soc., 140 (1993) 348
 - [3] K. von Rottkay, M. Rubin, Mat. Res. Proc. 403
 - [4] K. von Rottkay, M. Rubin, to be published in Mat. Res. Proc. 426
 - [5] M. Rubin, K. von Rottkay, S.-J. Wen, N. Ozer, and J. Slack, presented at the Int. Symp on Opt. Mater. Technol. (Freiburg, Germany, Sept 1996) and published in SPIE Proceedings
 - [6] S.-J. Wen, K. von Rottkay, M. Rubin, to be published in ECS Proceedings October 1996
 - [7] personal communication with Dr. J. Bell at the 2nd Int. Meeting on Electrochromics, San Diego, California, October 2, 1996
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