

A Simple Laboratory Demonstration of Electrochromism

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The ability of certain materials or chemical systems to respond to applied electrical fields or currents by changing color or optical density is called *electrochromism*. As this phenomenon may be an interesting and illustrative example of solid state reactions, we have included a laboratory exercise based on electrochromism in our course on inorganic materials chemistry for first-year students. This exercise can easily be carried out in one day by a group of two students, who are requested to construct an electrochromic cell consisting of a thin, transparent layer of WO_3 on a glass plate with a thin, transparent and conducting surface coating of doped SnO_2 . By electrolytic intercalation/decalation of hydrogen ions, performed in a beaker with sulfuric acid, a deep-blue color can be reversibly developed and removed in the WO_3 layer.

Technical Applications

Some electrochromic materials are potentially useful as coatings on windows and solar energy collectors (1). A strong driving force for current research is the possibility to design electrochromic displays, with thin layers generating the colored patterns. Today, the phenomenon is utilized commercially, for example, in rear view mirrors for cars, to reduce excessive reflected light by a dark shading induced by an electric signal (2).

The technique for deposition of thin layers on surfaces is well established in research and industry. However, methods such as CVD and sputtering, frequently used, are probably too elaborate for a university general chemistry course, and require sophisticated equipment, high vacuum, etc. The laboratory exercise described here is therefore based on a wet-chemical method for depositing the electrochromic WO_3 layer. It is likely to be qualitatively inferior to the high-tech methods, for example with regard to homogeneity of the layer, but has proved to be reliable and sufficiently good for successful demonstrations of electrochromism.

Chemical and Physical Basis

The induced coloration of WO_3 , when hydrogen (or alkali) ions enter the structure by electrolytic or chemical means, is due to creation of electron *donor* levels in the bandgap, which is about 3.5 eV in the pure, colorless (actually, pale yellow) WO_3 . These donor levels, about 1.4 eV below the conduction band, are associated with the defect sites arising when W^{6+} turns into W^{5+} , in order to maintain overall charge neutrality on ion insertion (2). By absorbing photons in the red part of the spectrum, electrons at the donor levels are excited to the conduction band, and this is the cause of the blue coloration in H_xWO_3 . At moderate dopant levels ($x < 0.3$) the insertion will be reversible, accompanied by just a minimal structural change from the original ReO_3 -type structure to a perovskite type (Fig. 1).

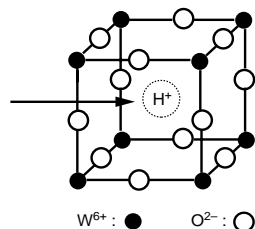


Figure 1. Idealized H_xWO_3 unit cell.

At higher x values, however, further structural rearrangements will occur, leading to other colors than blue and a slower decalation rate.

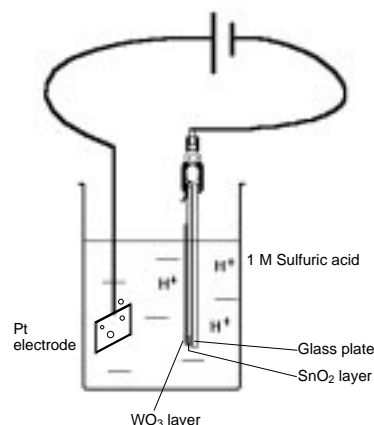


Figure 2. Electrolytic cell used to demonstrate electrochromism in WO_3 .

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Preparation of Layers

First, a conductive yet transparent coating must be put on the glass substrate, so that the electrons can be transferred to the WO_3 layer from an external source (Fig. 2). We used standard microscope object glasses as substrates and found that an Sb-doped SnO_2 layer can be deposited relatively easily on the cleansed glass surface by spray pyrolysis. The feed was a solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in water-ethanol (in weight proportions roughly 1:1:1) with a few mol % SbCl_3 added. More precise formulations for optimal performance of Sb- or F- doped coatings are given in refs 3 and 4. Tin(II) chloride could also be used, as the pyrolysis reactions occur in air. Some precipitation is unavoidable in the mixture, and should be given time to settle before spraying. For a discussion of the effects of varying dopant levels on the electrical and optical properties of SnO_2 , see ref 5.

Descriptions of various spray devices are found in the literature (e.g., 4, 6), and some of the less sophisticated designs with glass and PVC tubing could well be taken up by a skilled student. A crucial feature of the nozzle is that it should generate a fine spray and prevent larger droplets from reaching the pyrolysis zone next to the substrate. A simpler alternative, in fact the default solution in our course, is an artist's spray bottle. Preferably, it is clamped to a stand and connected to a bomb providing the driving gas (Fig. 3). It is imperative to perform the spray operation in a fume cupboard, allowing a distance of at least one meter between the nozzle and the hot glass plate, in order that only fine spray particles reach the glass. It is crucial for a successful pyrolysis that a correct substrate temperature (300–500 °C) is used (7). In fact, we never measured the temperature on our simple laboratory hot plate, but found the correct value by trial and error, usually at the highest or next highest stage. Too low temperatures resulted in white, unpyrolyzed and nonconducting spots cov-

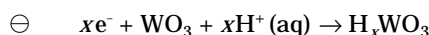
ering the glass. For a discussion of the relative importance of parameters such as temperature for the spray pyrolysis process, see ref 8.

Under ideal spray conditions a very thin, transparent coating is formed on the glass after 5–10 seconds. Spraying should be interrupted when bluish interference colors are seen from some angle of view. The ultimate proof of a useful SnO_2 layer is a reasonably low electric resistance, such as $100\ \Omega$ over 5 cm, which is easily checked by means of a multimeter. A higher value, say $1\ \text{k}\Omega$, may be acceptable but gives a slower coloration/decoloration rate in the final electrochromic device. Of course, careful cleaning of the fume cupboard will be necessary after the spray operation.

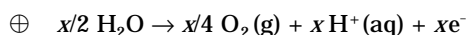
The WO_3 layer on the SnO_2 is conveniently deposited, as suggested in ref 9, from a solution of colloidal tungsten oxide, prepared by ion exchange in $\text{Na}_2\text{WO}_4(\text{aq})$. To this end we passed a 0.5-M tungstate solution slowly through an H^+ saturated DOWEX 50 WX2 resin (100–200 mesh) in a short (~5 cm), simple glass column. We advise against the use of complex columns such as comprising glass filters, where surface-induced gelation of the colloidal WO_3 is likely to occur. A few drops from the column are enough to cover a glass plate with a surface of about $10\ \text{cm}^2$. They can be smeared out manually, or better by the use of some centrifuge device, if available. A transparent, amorphous although stable WO_3 layer will develop after ca. 1 hour of drying at room temperature.

Cell Assembly and Test

The electrolytic cell depicted in Figure 2, comprising the $\text{SnO}_2(\text{Sb})/\text{WO}_3$ -coated glass plate and a small Pt foil as electrodes in a beaker with 1 M sulfuric acid as electrolyte, was used to demonstrate the electrochromic effect. The glass plate was clamped by a crocodile clip to a piece of graphite felt, in order to improve the electric contact with the SnO_2 layer. On applying 1–2 V over the electrodes, a deep blue coloration of WO_3 develops in a few seconds, due to partial reduction of W^{6+} and simultaneous H^+ insertion according to:



On the Pt foil tiny oxygen bubbles can be observed:



On reversing the polarity, the blue color bleaches and disappears in a few seconds. Provided only moderate voltages are applied, the process is reversible and can be repeated many times.

Student Results

So far none of our students have failed with preparation of the electrochromic device as sketched above, al-

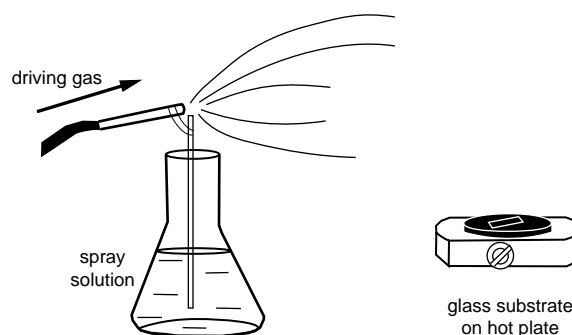


Figure 3. Setup used for coating of doped SnO_2 on glass plates.

though the quality with respect to homogeneity, transparency, and conductivity of the layers generally differed. The most tricky part is the spray operation, which sometimes failed initially, but always succeeded on a second attempt. Students should be advised to prepare their ion exchange columns properly. Excess acid, not carefully washed out, will cause formation of yellow tungstic acids, " H_2WO_4 ". Some effort should be made to smear out the WO_3 to a homogeneous layer on the glass, as thin as possible, to avoid subsequent cracking. To guarantee a successful demonstration of the electrochromic effect, a number of glass plates should be coated, as the quality of the WO_3 layer can be judged only after drying.

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