



## Electrochromism at Niobium Pentoxide Electrodes in Aqueous and Acetonitrile Solutions

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Display devices based on electrochromic effects on metal oxides are currently being investigated intensively. For example a number of studies on the electroreduction of  $\text{WO}_3$  to form the blue hydrogen tungsten bronze,  $\text{H}_x\text{WO}_3$ , which can be reversibly bleached upon oxidation have been reported (1-4). However the slow dissolution of  $\text{WO}_3$  in the aqueous sulfuric acid solutions used as the electrolytes in most cells has prevented application of this system to practical devices. Systems with  $\text{WO}_3$  based on nonaqueous solvents, such as glycerol and acetonitrile, with formation of H- or Li-bronzes have also been described (5-8), but these also have problems (dissolution, irreversible coloring, or slow response). We report here preliminary experiments demonstrating electrochromic behavior of  $\text{Nb}_2\text{O}_5$  in both aqueous and acetonitrile (AN) solutions. This oxide, which is insoluble in many media, shows reasonable response times and reversible coloring and bleaching, and so appears to be a promising system for electrochromic devices. Moreover the excellent stability of Nb towards corrosion in mineral acids because of the protective  $\text{Nb}_2\text{O}_5$  layer (9) suggests that this material should form stable systems.

The  $\text{Nb}_2\text{O}_5$  electrodes were prepared by heating a niobium metal disk (12.7 mm dia., cut from a rod of 99.8% Nb obtained from Alfa Ventron) in air to  $\sim 500^\circ\text{C}$  for about 10 min which produced a white layer of  $\text{Nb}_2\text{O}_5$  about 15  $\mu\text{m}$  thick. Electrical contact was made to the Nb metal by scraping off part of the oxide and connecting a Cu wire to the Nb with silver epoxy cement. A typical current-potential curve recorded with this electrode in 1 M  $\text{H}_2\text{SO}_4$  with a Pt wire as a counter electrode and vs. a  $\text{Hg}/\text{Hg}_2\text{SO}_4/1\text{ M } \text{H}_2\text{SO}_4$

reference electrode, is shown in Fig. 1. The cathodic current which started at  $\sim 0\text{ V}$  vs. NHE is associated with coloration of the  $\text{Nb}_2\text{O}_5$  layer and the anodic current, which appeared after reversal of the potential scan direction, is associated with the bleaching process. Upon reducing this electrode in the aqueous 1 M  $\text{H}_2\text{SO}_4$  with a potential step to  $-0.6\text{ V}$  vs. NHE, a dark blue color appeared on the electrode surface. The blue color disappeared upon oxidation by a step to  $+1\text{ V}$  vs. NHE. The electrochromic process was reversible with a response time of less than 1 sec.

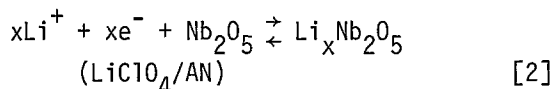
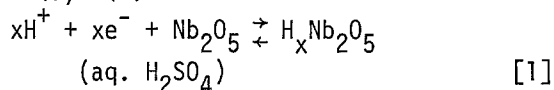
Electrochemical reduction and coloration of the  $\text{Nb}_2\text{O}_5$  electrode could also be carried out in AN solution containing 0.8 M  $\text{LiClO}_4$ . All solutions were prepared in an inert atmosphere glove-box by dissolving the  $\text{LiClO}_4$  (dried by heating under vacuum at  $110^\circ\text{C}$  for three days), in AN (distilled before use by a previously described procedure (10)). The electrochemical cell containing a Pt counter electrode and bleached  $\text{Nb}_2\text{O}_5$  quasi-reference electrode was filled in the glove box, then sealed with vacuum grease and removed for the electrochemical experiments. A current-potential curve of the  $\text{Nb}_2\text{O}_5$  electrode in the AN/ $\text{LiClO}_4$  solution is shown in Fig. 2. The cathodic current which started at about 0 V vs. the  $\text{Nb}_2\text{O}_5$  reference electrode is associated with coloration of the film. The electrode surface was bleached during passage of the anodic current which appeared following potential scan reversal. Upon stepping the electrode potential between  $-0.8\text{ V}$  and  $+1.5\text{ V}$  in these solutions, the electrode could be colored and bleached reversibly with a response time of 1 to 2 sec. Continuous coloring and bleaching (1 sec steps) was carried out three days with no apparent changes in behavior.

The  $\text{Nb}_2\text{O}_5$  appeared to be stable in the aqueous-sulfuric acid and the AN solutions

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under cycling and at open circuit, although in the case of the aqueous solutions some hydrogen evolution appeared during the coloration process.

While we have not yet investigated the mechanism of this reaction in any detail, as a working hypothesis we propose that the coloring process in aqueous and AN solutions occurs either by niobium bronze formation (by analogy to the tungsten bronzes) or by reduction of niobium(V) (9):



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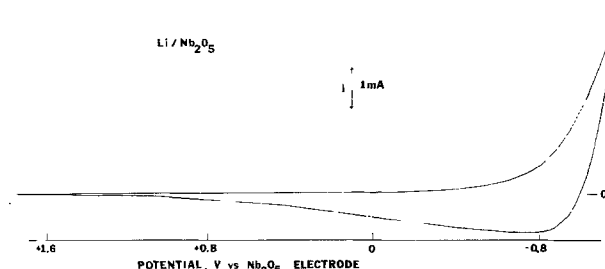


Fig. 2. Current-potential curve recorded with  $\text{Nb}_2\text{O}_5$  electrode in 0.82 M  $\text{LiClO}_4/\text{AN}$  solution; scan rate: 100 mV/sec.

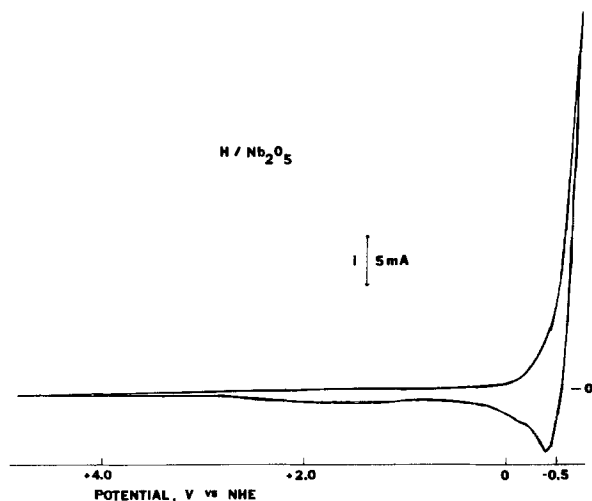


Fig. 1. Current-potential curve recorded with  $\text{Nb}_2\text{O}_5$  electrode in aqueous 1 M  $\text{H}_2\text{SO}_4$  solution; scan rate: 100 mV/sec.

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