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An electrochromic cell using a solid proton conductor

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An electrochromic cell with a solid proton conductor, $HUO_2PO_4 \cdot 4H_2O$, as the electrolyte is described and its performance was investigated.

1. Introduction

Recently, electrochromic cells (ECC cell) have received considerable attention for their use as display devices. The ECC cell is based on the reversible coloration of a tungsten (VI) oxide film [1]. In general, ECC cells reported previously have used an aqueous solution as the electrolyte and this has disadvantages such as leakage, freezing and volatilization of the electrolyte. Thus, the application of solid electrolytes in an ECC cell is of interest and solid state devices have been tested by some investigators [2, 3] using solid ion conductors such as $RbAg_4I_5$ [4], and β-Al_2O_3 [5].

In this paper, an ECC cell with a solid proton conductor, $HUO_2PO_4 \cdot 4H_2O$, as the electrolyte is described and its performance has been examined. The cell is

$$Ag|HUO_2PO_4 \cdot 4H_2O|WO_3, SnO_2$$

$HUO_2PO_4 \cdot 4H_2O$ was prepared by the method described in the literature [6]; X-ray and thermogravimetric analysis agreed with the reported data, and the electrical conductivity was comparable to that reported [7]. A mixture of $HUO_2PO_4 \cdot 4H_2O$ and Teflon powder (Mitsui Fluoro Chemicals, Teflon 6-J) (19 : 1 weight ratio) was pressed under a pressure of 2000 kg cm^{-2} to form a pellet 1–3 mm in thickness and 13 mm in diameter. The Teflon powder was used to give flexibility to the tablet and to make good contact with the WO_3 film. The 1 kHz a.c. conductivity of the tablet at room temperature was 1.3×10^{-4} $(\Omega\,cm)^{-1}$. The thin film of WO_3 (about 1 μm thick) was deposited by vacuum evaporation onto a glass substrate (18 x 18 x 1.5 mm) which was already coated with conducting tin oxide. The construction of the ECC cell is shown schematically in Fig. 1.

The cell was pale yellow, the colour of the $HUP_2PO_4 \cdot 4H_2O$, and the cell resistance was about 1 kΩ. On applying a d.c. potential of about 1 V across the cell and the WO_3 as the cathode, the colour changed to blue due to the formation of H_xWO_3 [8]. The maximum value of x in these

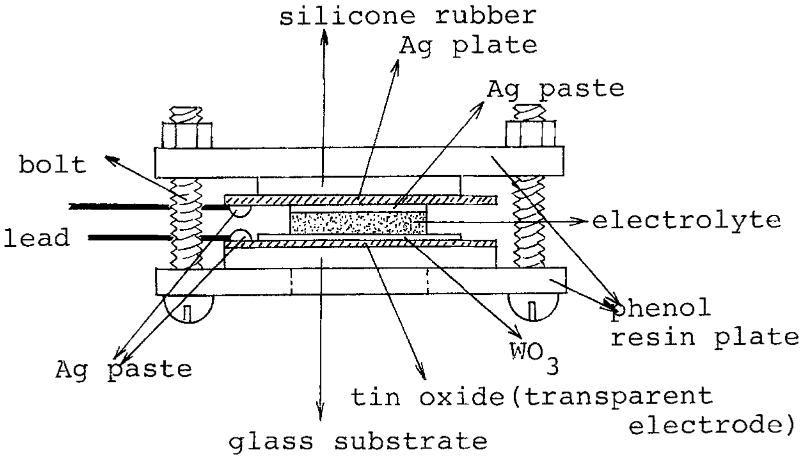

Fig. 1. Schematic diagram of the ECC cell.

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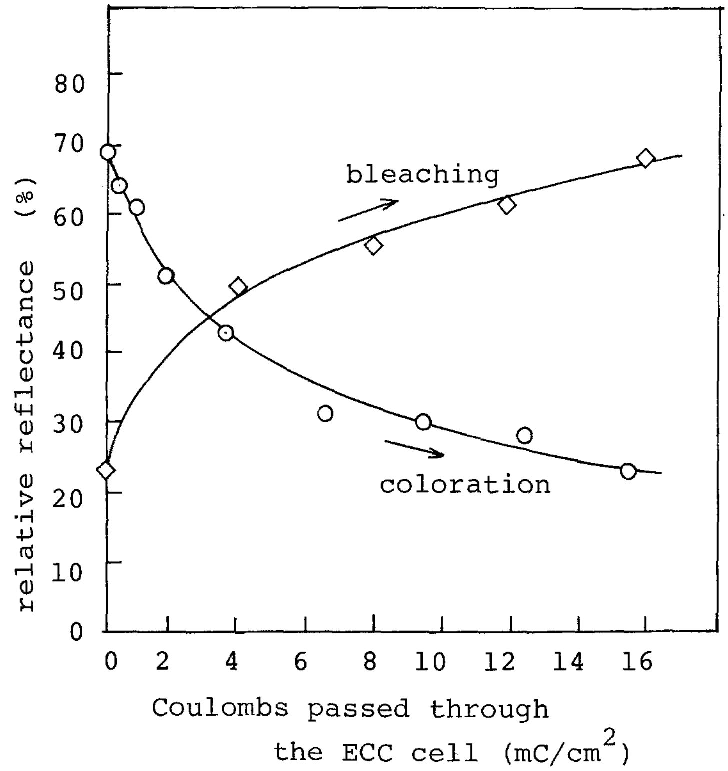

Fig. 2. The relation between the relative reflectance and the coulombs passed through the cell.

experiments was 0.05, according to a theoretical calculation of the coulombs passed through the cell. On reversing the applied potential, the blue colour disappeared. Photographs of the cell were taken with the help of a colour film after passing a current through the cell for a period of time, and the relative reflection intensities of the colour prints were measured with a spectrometer (Beckman, DB-G type) at $\lambda = 724$ nm; the white part of the colour prints was taken as the standard. The relation between the relative reflectance and the coulombs passed through the cell is shown in Fig. 2. As shown in this figure, a reversible colour change is obtained. The cyclic performance tests of this ECC cell were carried out with a square wave of 1 Hz at an applied potential of about 3 V and an initial current density of about 3 mA cm^{-2}. The cell broke down after operating for three weeks, a period which corresponds to about two million cycles of the colouring and bleaching process. The cell resistance increased with time. The breakdown of the cell may be due to the electrochemical decomposition of the electrolyte, during the period of the off-voltage of the square wave.

Although a great deal of improvement is necessary before this type of ECC cell could become commercially available, this cell may be promising as a practical display device.

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