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Electrochromics for energy efficient buildings: Towards long-term durability and materials rejuvenation☆

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ABSTRACT

Electrochromic devices such as "smart windows" for energy efficient windows must be durable enough for many years of practical use. Typical devices employ films based on W oxide and Ni oxide, and this paper surveys recent progress on durability-related issues for these materials. In the case of W oxide, we discuss the beneficial effects of Ti addition, and we describe recent and unexpected progress concerning galvanostatic rejuvenation of aged W oxide films. For Ni oxide, we report how charge exchange declination during extended voltammetric cycling can be modeled in terms of a power law.

1. Introduction

A large part of the primary energy in the world is spent in buildings. The fraction is as large as 30–40% on a world-wide scale and the energy is used for heating, cooling, lighting and appliances [1]. Furthermore, the portion that goes into buildings tends to increase, particularly in the more affluent countries, and recent numbers for the US indicate specifically 34, 36, 38 and 41% for 1980, 1990, 2000 and 2010, respectively [2]. Most of the energy comes from coal, oil and gas and leads to emission of carbon dioxide into the atmosphere, which in its turn yields global warming and rising sea level [3] and may even lead to vast secondary effects such as political unrest [4].

The buildings sector is notorious not only for wasting immense amounts of energy but also for its huge savings potential. By and large, these savings are an untapped resource, which is due to poor but thoroughly entrenched building practices [5]. Glazings, denoting windows and glass facades, are particularly important in this connection and often act as weak links in the buildings' energy systems and let through too much thermal and solar energy, so that energy guzzling air conditioning must be used to create a comfortable indoor climate.

The glazings can be very significantly improved by implementing "green" technology and optimize the flows of solar energy and visible light, while the thermal insulation is kept as large as possible [6]. In particular, it is important to regulate the transmittance of solar energy and light through the glazings in accordance with dynamic needs and human desires, which is feasible by the use of chromogenic materials whose optical transmittance responds to an external stimulus such as ultraviolet irradiation (photochromic materials), temperature (thermochromic materials), or electrical voltage or current (electrochromic materials, incorporated in electrochromic devices) [7,8]. This paper deals with electrochromic (EC) materials and devices; their state-of-the-art with regard to glazings was summarized recently [9–12]. Below we summarize some recent studies with emphasis on basic work related to long-term durability and material rejuvenation [13–15], which obviously are important subjects with regard to applications. For detailed descriptions, we refer to the original publications.

2. Electrochromic device designs and functioning principles

There are several different types of EC devices [11], but the ones that are presently discussed and implemented as "smart windows" in buildings are of the type illustrated in the right-hand part of Fig. 1 [16–18]. The center of the device consists of a transparent electrolyte, which can be a polymer layer or an oxide thin film, which joins two EC thin films typically based on strongly disordered tungsten oxide and nickel oxide [19]. This three-layer arrangement is located between transparent electrical conductors, which in most cases are heavily doped wide band-gap oxides such as In_2O_3:Sn (known as ITO), SnO_2:F or ZnO:Al (although many other options exist, including coinage-metal-based ones). When a voltage, typically ~2 V dc, is applied between the transparent conductors, there is an exchange of ions and charge-balancing electrons between the films of W oxide and Ni oxide. Both of these films are dark when the charge resides in the W oxide whereas both of the films are bleached when the charge is in the Ni oxide, which implies that the overall optical transmittance can be varied. The

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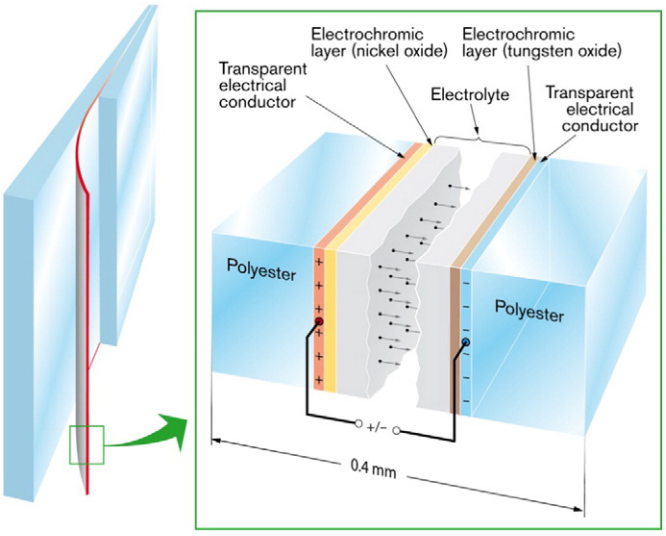

Fig. 1. Principle of a foil-type EC device and its implementation as a laminate between glass panes in "smart windows" for energy efficient buildings.
From Bayrak Pehlivan et al. [18].

ions in the electrolyte should be small in order to allow facile charge transport and thereby rapid changes of the optical properties, and protons (H^+) or Li^+ are normally used. We note that EC films of W oxide and Ni oxide are different with regard to their electrochemistry, and ions are able to enter into the lattice structure of W oxide, whereas electrochemical surface reactions are dominating for Ni oxide films in Li^+-conducting electrolytes [20]. Metallic bus bars on at least parts of the circumference of the EC device are usually needed in order to accomplish charge equilibration and uniform coloration.

The functioning of the EC device can be resembled to that of a thin-film battery whose charging state corresponds to a degree of optical absorption. The EC device, just as the battery, can maintain its properties for days or more under open-circuit conditions provided that the centrally positioned electrolyte has low enough electron conduction—which is normally the case for polymer electrolytes but not for inorganic thin-film electrolytes. The fact that charge is needed only to alter the properties leads to highly energy-efficient operation of "smart windows".

The battery-type EC device can be constructed in several principally different ways. Most work has been devoted to a "monolithic" arrangement with five superimposed thin films on a single glass pane. Such a design allows, in principle, large-scale in-line production in the same way as for today's metal-based solar-control and low-emittance coatings [21]. The EC devices produced in this way are delicate and should, for practical reasons, be integrated in EC glazings in conjunction with the coating manufacturing. The need for bus bars necessitates device fabrication in predetermined dimensions. An alternative to the monolithic construction, which was introduced some years ago [22,23] and is illustrated in the left-hand part of Fig. 1, makes the EC device as a flexible two-component foil embodying one foil of polyethylene terephthalate (PET) coated with ITO and W oxide, another foil of PET coated with ITO and Ni oxide, and lamination by the use of a transparent polymer electrolyte joining the films of W oxide and Ni oxide. This "double foil" can then be used for glass lamination using standard procedures involving polyvinyl butyral (PVB) or ethylene-vinyl acetate (EVA). The foil-based production strategy allows low-cost roll-to-roll deposition [24] and can be combined with "free-form" device manufacturing using post-prepared bus bars. Hence the EC functionality can be separated from the glazing manufacturing, which permits entirely different business models for monolithic and polymer-laminated EC "smart windows".

3. W-oxide-based films: general considerations, and improved cycling durability by Ti addition

Long-term durability is an obvious requirement for EC devices to be used in "smart windows", and this property has been the subject of numerous studies in particular with regard to device performance and industry aspects; much of this work appeared already in the late 1990s [25–29]. Durability is a multifaceted property and involves the

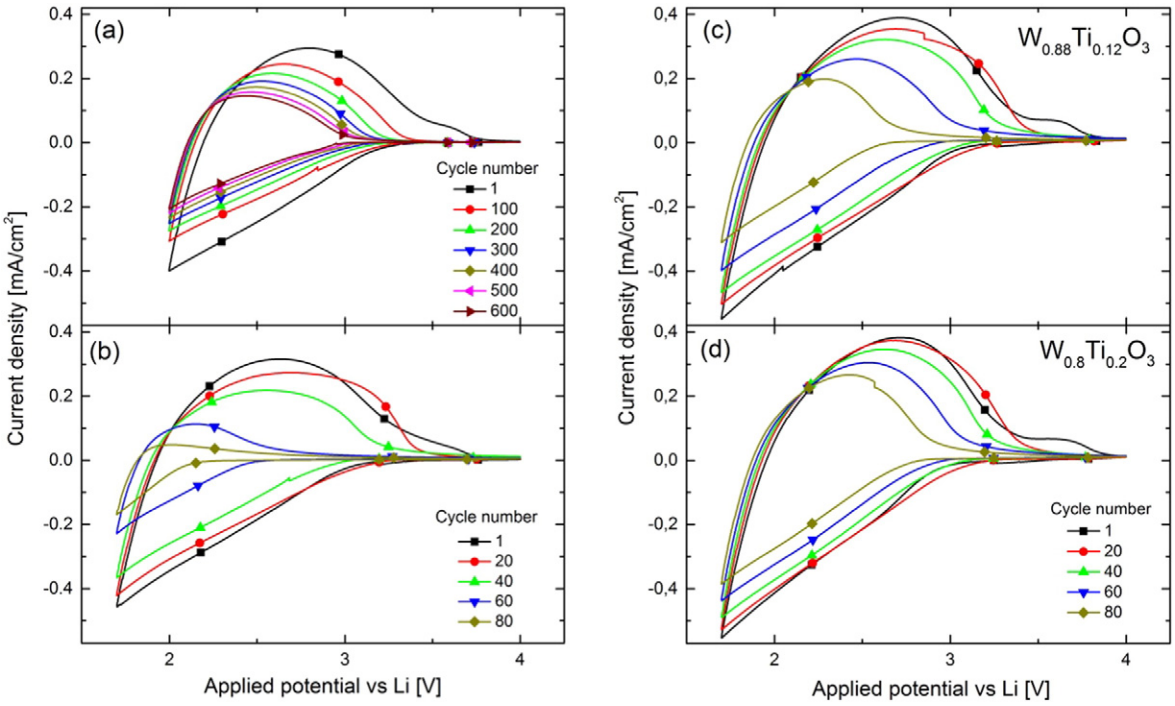

Fig. 2. Cyclic voltammograms for ~300-nm-thick films of (a, b) W oxide and (c, d) W–Ti oxide with the shown compositions. Data were taken after the indicated number of CV cycles for voltage sweeps at 10 mV/s at 2.0–4.0 or 1.7–4.0 V vs. Li^+/Li.
From Arvizu et al. [13].