



Short Communication

CaF₂: A novel electrolyte for all solid-state electrochromic devicesXi Chen^a, Hulin Zhang^a, Wenjie Li^b, Yingjun Xiao^b, Xiang Zhang^{a,*}, Yao Li^{a,**}^a Center for Composite Materials and Structure, Harbin Institute of Technology, Harbin, 150001, PR China^b School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, PR China

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ABSTRACT

The energy consumption in building ventilation, air, and heating conditioning systems, accounts for about 25% of the overall energy consumption in modern society. Therefore, cutting carbon emissions and reducing energy consumption is a growing priority in building construction. Electrochromic devices (ECDs) are considered to be a highly promising energy-saving technology, due to their simple structure, active control, and low energy input characteristics. At present, H⁺, OH⁻ and Li⁺ are the main electrolyte ions used for ECDs. However, H⁺ and OH⁻ based electrolytes have a high erosive effect on the material surface and have a relatively short lifetime. Li⁺-based electrolytes are limited due to their high cost and safety concerns. In this study, inspired by prior research on Ca²⁺ batteries and supercapacitors, CaF₂ films were prepared by electron beam evaporation as a Ca²⁺-based electrolyte layer to construct ECDs. The structure, morphology, and optical properties of CaF₂ films were characterized. ECDs with the structure of ITO (indium tin oxide) glass/WO₃/CaF₂/NiO/ITO show short switching times (22.8 s for the coloring process, 2.8 s for the bleaching process). Additionally, optical modulation of the ECDs is about 38.8% at 750 nm. These findings indicate that Ca²⁺ based ECDs have the potential to become a competitive and attractive choice for large-scale commercial smart windows.

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1. Introduction

The energy consumption in building ventilation, air, and heating conditioning systems accounts for about 25% of the total energy consumption in our society [1–3]. Among various technologies, smart windows provide an effective and feasible solution for improving a building's energy efficiency by altering the transmittance and absorbance of light [1,3–5]. The most promising candidates for smart windows are electrochromic devices (ECDs), which can reversibly change the optical property by applying voltage [6,7]. The properties of ECDs are determined by the insertion and extraction of electrolyte ions during electrochemical reaction processes [8,9]. Currently, Li⁺-based electrolytes are the most widely used and effective electrolytes in ECDs [10–14]. Despite the successful commercialization of Li⁺-based ECDs, safety concerns of Li-salts during preparation processing and limited Li resources are a challenge for widespread Li⁺-based ECD use in smart windows [6,15–17]. Therefore, it is important to explore a

new generation of naturally abundant and low-cost electrolytes for ECDs.

Calcium is the fifth most abundant element in the Earth's crust and exhibits a high theoretical electrochemical capacity [18,19]. Compared to other multivalent ions, Ca²⁺ has a low polarization strength, similar to Li⁺, and therefore holds promise for fast reaction kinetics and good electrochemical performance [20–23]. Moreover, thanks to their low cost and reduced safety concerns, compared to Li⁺-based systems, Ca²⁺-based electrochemical systems have been extensively investigated in batteries and supercapacitors [20–25]. Following previous research on Ca²⁺ batteries and supercapacitors [20–25], Tong et al. [26] assembled a novel and safe aqueous Ca²⁺ electrochromic battery, which demonstrated high stable, high-rate capability, a high energy density, and greenish-yellow to black electrochromism. However, to our knowledge, this is the first study on Ca²⁺-based electrochromism aimed at developing safe, low-cost, and green Ca²⁺-based ECDs.

CaF₂ is a promising solid-state electrolyte, due to its superior chemical and physical stability [27,28], high ionic conductivity [29], and high transparency ranging from ~150 nm to 12 μm [30,31]. Electron beam evaporation is a fast, environmentally friendly, and economical method to prepare high quality homogeneous thin

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films. In this paper, CaF₂ films were prepared by electron beam evaporation as the Ca²⁺-based electrolyte layer to construct the ECDs with the structure of ITO glass/WO₃/CaF₂/NiO/ITO. Additionally, the structure, morphology, and optical properties of CaF₂ films were characterized. The electrochromic (EC) performances of these devices were evaluated by coloring at -2.5 V for 30 s and bleaching at 2.5 V for 20 s via *in situ* transmittance recording. More importantly, the optical modulation (38.8% at 750 nm) is comparable to Ca²⁺-based liquid state ECDs [26], and the switching times (22.8 s for coloring and 2.8 s for the bleaching) are shorter than many of the previously reported Li⁺-based solid-state ECDs.

2. Materials and methods

2.1. Deposition of CaF₂ films

The silica glasses substrates were ultrasonically cleaned in deionized water followed by alcohol, for 10 min each. The CaF₂ films were prepared by electron beam evaporation using CaF₂ particles with a diameter of ~1–3 mm. The detailed conditions of CaF₂ film preparation are provided in Table S1. After evaporation, the CaF₂ films were annealed at 200 °C for 60 min in a muffle furnace to improve film adhesion.

2.2. Deposition of the ECD

ITO glass with an average transmittance of 80% and a sheet resistance of 10 Ω were used as the substrate. All layers of the ECDs were deposited by electron beam evaporation. The detailed parameters of WO₃, NiO, and top ITO layers follow our previously reported method [10,12,15] and are given in Table S1. The deposition of each layer was performed continuously with pre-evaporation for 10 min before each deposition. After evaporation, the ECDs were annealed at 200 °C for 60 min in a muffle furnace to enhance the electrical and optical properties of the top ITO films.

2.3. Characterization

The surface and cross-section morphologies were characterized using scanning electron microscopy (SEM, Merlin Compact, Zeiss, Germany). The surface roughness of CaF₂ film was characterized by Atomic Force Microscope (AFM, Dimension Fastscan, Bruker, Germany). The crystalline structure of the CaF₂ film was characterized by X-ray diffraction (XRD, X'Pert, Panalytical, Netherlands) in the 2θ range of 10°–80°. The transmittance spectra of the CaF₂ film were characterized by UV-Vis-NIR optical spectroscopy (Lambda 1050, PerkinElmer, USA). The EC performances of ECDs were investigated with a combination of a Vis-NIR fiber optic spectrometer (Maya 2000-Pro, Ocean Optics, USA) and an electrochemical station (CHI 660E, Chenhua, China).

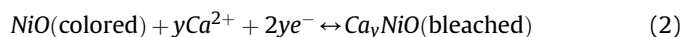
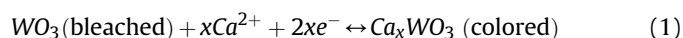
3. Results and discussion

The performances of CaF₂ films are strongly dependent on their structure, morphology, and optical properties. As shown in Fig. 1a, there is a broad peak and two diffraction peaks in the XRD pattern of the CaF₂ film. The broad peak in the range of 15–25° can be assigned to the silica glass substrate [15]. Peaks located at 28.2° and 47.0° represent the (111) and (220) planes of CaF₂ cubic structure (JCPDS Card (No. 35-0816)) [31]. The surface morphology of the CaF₂ films, shown in Fig. 1b, are composed of particles with uniform size, which is favorable for ion transportation. As depicted in Fig. 1c, the CaF₂ film shows a high transmittance, over 90%, from 250 to 2500 nm, which is necessary for the electrolyte layer [32]. The AFM image of the CaF₂ film is presented in Fig. 1d. The root mean square

surface roughness is approximately 0.6 nm and, thus, the CaF₂ films can effectively avoid short circuits [33,34].

Fig. 2a shows the schematic diagram of the ECD, which is similar to our previously reported Li⁺- and Mg²⁺-based ECDs. The cross-sectional image, with thickness of each layer of the solid-state ECD, is shown in Fig. 2b. The device exhibits a five-layer structure and the thicknesses of WO₃, CaF₂, NiO and top ITO films consistent with the setting values, which are 325, 185, 175, and 160 nm, respectively. The identified interfaces between the CaF₂ film and EC films are favorable for ion transportation and suggest these layers are physically stable with no interfacial reaction [10,15]. The vague interface between EC films and ITO films is mainly ascribed to the interdiffusion of their similar surface morphologies [15], which are favorable for charge transportation [35].

As shown in Fig. S1, the ECDs are coloring at -2.5 V for 30 s and bleaching at 2.5 V for 20 s. Fig. 3a displays the transmittance spectra at the colored and bleached states of the all solid-state ECDs, with corresponding digital photos in Fig. S2. The ionic conductive mechanism of CaF₂ in ECDs is similar to Li⁺-based ECDs [36]. The intercalation and extraction of Ca²⁺ ions and electrons between the WO₃ film and NiO film can be described by:



When a negative voltage is applied to the ECD, the Ca²⁺ ions extract from NiO films and insert into WO₃ films, and the ECD changes to the colored state. When applying a positive voltage, the Ca²⁺ ions extract from WO₃ films and insert into NiO films, and the ECD changes to the bleached state. The ECD optical modulation (ΔT) is determined by:

$$\Delta T = T_b - T_c \quad (3)$$

where T_b and T_c are the transmittance of the ECD for the bleached state and colored state, respectively. As illustrated in Fig. 3a, the maximum ΔT is 38.8% at 750 nm, where the T_c and T_b are 39.6% and 78.4%, respectively. As depicted in Table S2, the ΔT in this study is comparable to Ca²⁺ based ECDs and less than most Li⁺-based ECDs. This is attributed to the higher valence of Ca²⁺ and the greater electrostatic force between Ca²⁺ and the frame.

Switching time, which is the time required to achieve 90% of total transmittance variation between two states [37,38], was examined to further evaluate the ECD performance. As shown in Fig. 3b, monitoring the transmittance change at 600 nm, the coloring and bleaching switching times of ECD were 22.8 s and 2.8 s, respectively. Notably, the coloring process takes longer than the bleaching process, which is caused by the greater electrostatic force between Ca²⁺ and EC layer [39] arising from the higher valence and larger ionic radius of Ca²⁺. Regardless, the switching times of the ECD are shorter than most other all solid-state inorganic ECDs (Table S2) and comparable to reported ECDs using gel electrolytes [40].

The *in situ* transmittance measurements of the ECD during multiple potentials at 600 nm are presented in Fig. S3. The transmittance of the bleached state fluctuates slightly and stabilizes around 81%. The transmittance of the colored state increases from 44% at the first cycle to 58% at the 125th cycle and then remained stable, which is the result of the different types of ions intercalation. According to a prior study [41], there are two different types of ion intercalation for WO₃; shallow ones that are reversible and easy to insert and extract, and deep ones that are difficult to access and wherein ions become permanently trapped. The ionic radius of the Ca²⁺ (0.099 nm) is bigger than that of Li⁺ (0.06 nm), which can lead to much deep ion intercalation in WO₃ and poor cyclic stability. The

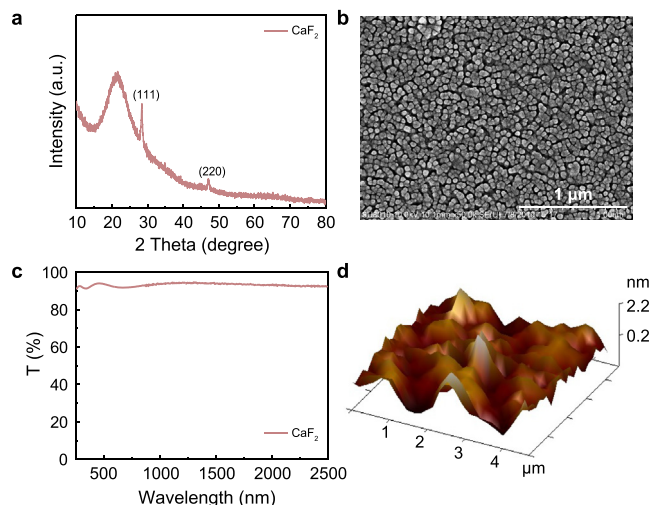


Fig. 1. Characterization of CaF₂ films: **a**, XRD pattern; **b**, SEM micrograph; **c**, Transmittance spectra; and **d**, AFM surface 3D image.

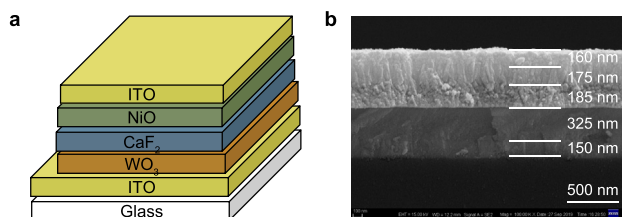


Fig. 2. All solid-state ECD: **a**, Schematic diagram and **b**, Cross-sectional image.

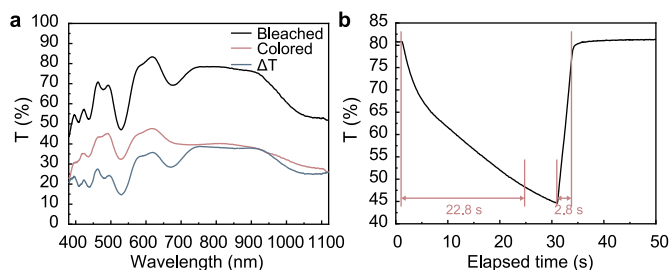


Fig. 3. **a**, Transmittance spectra of the ECD at different states and optical modulation during initial cycles. **b**, In situ transmittance spectra at 600 nm (30 s for coloring and 20 s for bleaching).

cyclic stability is closely related to the size of insertion ions and, the composition and microstructure of the EC materials. Therefore, WO₃ can be doped with other elements (e.g. V, Ta, and Mo) or prepared with suitable porosity for future work aimed at enhancing the cyclic stability of ECDs [1].

The coloration efficiency (CE) is an important criterion to evaluate the performance of ECDs, representing the change in the optical density (ΔOD) per unit charge density (ΔQ). It can be calculated according to the following equations:

$$\Delta OD = \text{Log}(T_b / T_c) \quad (4)$$

$$\Delta Q = \int j dt \quad (5)$$

$$CE = \Delta OD / \Delta Q \quad (6)$$

where T_b and T_c are the transmittances of the ECD in the bleached and colored states at 600 nm, ΔQ represents the intercalation charge density. As shown in Fig. S4, the calculated CE value of ECD is 52.4 cm² C⁻¹, which is larger than that of some reported Li⁺ and Mg²⁺ based all solid-state ECDs [15,42]. These results indicate that CaF₂ films have great potential to be used as inorganic electrolytes for the next generation of all solid-state ECDs.

4. Conclusions

CaF₂ films are successfully prepared by electron beam evaporation for use as the Ca²⁺-based electrolyte layer to construct ECDs. The structure, morphology, and optical properties of CaF₂ films are characterized. The ECD shows a five-layer structure ITO/WO₃/CaF₂/NiO/ITO and short switching times (22.8 s for the coloring process and 2.8 s for the bleaching process). Additionally, the optical modulation of the ECDs is approximately 38.8% at 750 nm. This study demonstrates Ca²⁺ based electrolyte is a promising alternative for an easily produced and environmentally friendly electrolyte to be used in EC smart windows.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.es.2022.100164>.

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