Sandwich Structured Electrolyte of High Sputtering Efficiency for All-solid-state Electrochromic Devices by Optical Design

JIA Hanxiang1,2, SHAO Zewei1,2, HUANG Aibin1, JIN Pingshi1, CAO Xun1
(1. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: The all-solid-state electrochromic devices (ECDs) have been widely developed for energy-saving windows, screen displays, multi-functional energy storage devices due to their characteristics such as large optical contrast, fast switching speed and good cycle stability. However, traditional all-solid-state ECDs based on monolayer electrolyte system are often limited by ordinary optical transmittance and inadequate sputtering efficiency. Herein, the all-solid-state ECDs integrated with LiAlO$_x$/Ta$_2$O$_5$/LiAlO$_x$ (ATA) sandwich structured electrolyte were successfully fabricated by reactive DC magnetron sputtering technique. By means of introduction of ATA sandwich structured electrolyte, the prepared ECDs with seven layer (ITO/NiO/LiAlO$_x$/Ta$_2$O$_5$/LiAlO$_x$/WO$_3$/ITO) was endowed with superfine optical transmittance and substantial sputtering efficiency simultaneously. The ATA-based ECDs realized satisfactory coloration efficiency of 79.6 cm$^2$/C, fast switching speed as short as 1.9 s for coloring and 1.6 s for bleaching, and excellent cycling stability over hundreds of cycles. Furthermore, ATA sandwich structured electrolyte makes full use of the excellent ionic conductivity and stability of Ta$_2$O$_5$, as well as enough lithium ions to meet the demand for fast color switching. Hence, ATA-based all-solid-state ECDs by continuous DC sputtering is expected to provide effective guidance for the mass production and practical application of the high-performance ECDs.

Key words: inorganic all-solid-state; electrochromic device; multilayer electrolyte; sputtering efficiency; optical design

With the enhancement of people's awareness of energy conservation and environmental protection, electrochromic devices (ECDs), used in buildings and vehicles have attracted increasing attention in recent years[1-2]. Compared to other chromogenic materials, electrochromism is capable of reversibly switching between colored and bleached states corresponding to internal ion inserting and extracting[3-4]. Taking advantage of that, ECDs play a major role in many fields, such as image display[5], smart windows[6] and stealth[7], which are expected to realize industrialization ahead of other chromogenic materials. However, the application of ECDs are limited due to their low fabrication efficiency, unaffordable cost and complex packaging technique. Therefore, study on all-solid-state ECDs with both high performance and high sputtering efficiency has gradually become a trend[8-10].

Some metrics are important factors affecting the performance of all-solid-state ECDs, such as optical contrast, cycle stability, especially sputtering efficiency and switching speed[11]. Inorganic all-solid-state ECDs are typically composed of five superimposed layers[12]: electrolyte layer is laminated between two EC layers, such as cathodic colored WO$_3$ and anodic colored NiO, individually connected with a transparent conductive layer. However, such typical five-layer ECDs based on monolayer electrolyte system are often limited by ordinary optical transmittance and inadequate sputtering efficiency, which is adverse to practical application and mass production. Generally, the magnetron sputtering efficiency of ceramic target with RF power supply is...
unsatisfactory\[^{[13-14]}\]. In contrast, there are few reports about solid electrolyte sputtered directly by metal or alloy targets, which can be applied to large-scale coating process\[^{[15]}\]. Furthermore, low optical transmittance of traditional all-solid-state ECDs is sometimes far from meeting the standards for practical applications\[^{[16-17]}\]. Optical design for anti-reflection simulation of multilayer electrolyte film can be applied to realize the theoretical maximum value of optical transmittance\[^{[18]}\]. Therefore, it is necessary to develop ECDs with a given multilayer structure which have high sputtering efficiency, high optical transmittance and satisfactory service performance\[^{[19-20]}\].

Taking the above factors into consideration, LiAlO\(_x\)/Ta\(_2\)O\(_5\)/LiAlO\(_x\) (ATA) sandwich structured electrolyte with LiAlO\(_x\) supplying enough lithium ions and Ta\(_2\)O\(_5\) serving as ion transport layer is requisite for optimizing the properties of the novel structured ECDs. The electron-blocking behavior, high ionic conductivity and chemical stability of Ta\(_2\)O\(_5\) makes it an ideal ion transport layer in ECDs. Meanwhile, LiAlO\(_x\) holds both high optical transmittance and high ionic conductivity. Due to the difference of refractive index between LiAlO\(_x\) and Ta\(_2\)O\(_5\), the sandwich structure electrolyte with alternating high and low refractive index can be designed, which is expected to improve the transmittance using the anti-reflection principle\[^{[21]}\]. Thus, the structure makes full use of the excellent ionic conductivity and stability of Ta\(_2\)O\(_5\), as well as enough lithium ions to meet the demand for fast color switching.

In this study, a seven-layer all-solid-state ECD (ITO/NiO/LiAlO\(_x\)/Ta\(_2\)O\(_5\)/LiAlO\(_x\)/WO\(_3\)/ITO) incorporated with ATA sandwich structured electrolyte of high sputtering efficiency, high optical transmittance and satisfactory coloration efficiency was designed. Due to effective lithium ions immigration channels provided by ATA sandwich structured electrolyte, the ECD hires remarkably improved switching speed and optimized optical transmittance. Moreover, the sputtering efficiency of ECDs was greatly improved by means of DC continuous magnetron sputtering using metal or alloy targets. The ATA based all-solid-state ECDs by optical design bring a further insight into the mass production and marketization of high-performance ECDs.

## 1 Experimental

### 1.1 Materials and synthesis

NiO film and LiAlO\(_x\)/Ta\(_2\)O\(_5\)/LiAlO\(_x\) sandwich structured electrolyte were deposited on 20 mm×20 mm indium tin oxide (ITO) glass substrates in sequence via reactive DC magnetron sputtering. LiAlO\(_x\) film was conducted in the flow of Ar/O\(_2\) (40 sccm/10 sccm). The sputtering used Li-Al alloy target (99.9%, diameter of 10.16 cm) with 200 W DC power for 45 min at room temperature (RT). Then the middle layer of Ta\(_2\)O\(_5\) was deposited at RT using Ta metal target (99.9%, diameter of 10.16 cm). The sputtering was performed under the condition of 200 W DC power and Ar/O\(_2\) ratio of 45:5. For the next step, an amorphous WO\(_3\) film was deposited in quick succession. Finally, a layer of ITO film was deposited on top of it acting as a top electrode. The detailed deposition parameters of each layer was simulated for max optimization of optical performance in Table 1.

### 1.2 Characterizations

The section microstructure of ECDs was shown in the cross-section micrographs by field-emission scanning electron microscope (FESEM, FEI Magellan 400). To monitor the surface roughness of monolayer electrolyte film, atomic force microscope (AFM, SII Nano Technology Ltd, Nanonavi Π) was examined. Later, the electrochromic property indexes including coloration efficiency, optical contrast, and cycle durability were studied by a CS350 electrochemical workstation (Corrtest, Wuhan). Lastly, UV/Vis/NIR Spectrometer (Hitachi, UV-4100) was used to characterize the in-situ transmittance spectrum of ECDs ranging from 350 to 2600 nm with the scanning speed of 1200 nm/min. In addition, optical modeling was executed via software of Essential MacLeod to optimize the experimental spectra, based on the theory of optical interference by utilizing the optical constants of LiAlO\(_x\) and Ta\(_2\)O\(_5\).

## 2 Results and discussion

### 2.1 Designed microstructure of ECDs

The surface microstructure of as-prepared electrolyte was characterized by AFM. The as-deposited LiAlO\(_x\) and Ta\(_2\)O\(_5\) films exhibited smooth surface with root-mean-square roughness (RMS) of 0.45 and 1.14 nm, respectively (Fig. 1(a-b)). The ECD containing LiAlO\(_x\)/Ta\(_2\)O\(_5\)/LiAlO\(_x\) sandwiched electrolyte was fabricated by optical optimization design. The film thickness, local enlarged view and corresponding element distribution of each layer in ECDs can be observed in Fig. 1(c, d, f). In Fig. 1(f), the element distribution diagram corresponds

| Layer | Target | Pressure/Pa | Power/W | Thickness/nm |
|-------|--------|-------------|---------|--------------|
| LiAlO\(_x\) | Li-Al | 2.0 | 40 : 10 | 200 | ~100 |
| Ta\(_2\)O\(_5\) | Ta | 0.7 | 45 : 5 | 200 | ~200 |
| LiAlO\(_x\) | Li-Al | 2.0 | 40 : 10 | 200 | ~100 |
| WO\(_3\) | W | 1.0 | 47 : 3 | 70 | 400 |
| NiO | Ni | 1.0 | 40 : 10 | 100 | 150 |
| ITO | ITO | 0.3 | 100 : 0 | 140 | 400 |

a: Upper layer; b: Lower layer
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Fig. 1  AFM image of LiAlO$_x$ layer (a) and Ta$_2$O$_5$ layer (b) of sandwich structured electrolyte (ATA), cross-section SEM image of ATA (c) and partial enlarged detail of it (d), surface SEM image of ATA (e), and element distribution of cross-section of ECDs (f)

to intuitive expression for the cross-section EDS of ECDs, which represented the element distribution of each layer collated with the SEM photographs in Fig. 1(c). The three middle layers consist of LiAlO$_x$/Ta$_2$O$_5$/LiAlO$_x$ sandwich structure with the thickness of nearly 100, 200 and 100 nm, respectively. Besides, surface SEM image of ATA electrolyte display the view of isolated island particles (Fig. 1(e)), which indicates the loose porous structure of LiAlO$_x$ layer. Thus, the ATA electrolyte constructed the effective conductive channel, which made the most of its excellent properties of ion conduction and stability.

2.2 Optical characterization and simulation of ECDs

To study O$_2$ flow ratio dependent optical transmittance of Ta$_2$O$_5$, different O$_2$ contents (O$_2$/(Ar+O$_2$)) (0, 5%, 10% and 15%) were set for Ta$_2$O$_5$ sputtering in Fig. 2(a). When the O$_2$ ratio corresponded to 10%, its optical transmittance was best optimized, which was applied to the sputtering of ATA electrolyte. Fig. 2(b) shows the in-situ transmittance spectra during 350–2600 nm with the applied voltage varying from –3 V to 3 V for ECDs. The initial state was highly bleached. With the increase of positive voltage, the optical transmittance decreased gradually due to its EC coloration effect. Until the bias reaches 3 V, the optical transmittance decreased even below 10%. Especially, ECDs presented excellent color retention as the external voltage was removed. Finally, ECDs returned to its original bleached state when the reverse voltage was applied.

In addition, optical simulation was performed for LiAlO$_x$/Ta$_2$O$_5$/LiAlO$_x$ sandwich structured electrolyte. The optical constants ($n$ and $k$) of LiAlO$_x$ and Ta$_2$O$_5$ were used for calculation, which was made for different thickness combinations of LiAlO$_x$ and Ta$_2$O$_5$, and an optimized structure was chosen upon the maximum integrated luminous transmittance. Then the experimental and
calculated transmittance spectra of sandwich structured electrolyte were tested (Fig. 2(c-d)), which fit well with each other. By means of the optical calculation via software of Essential Macleod, the optical transmittance of ATA reach over 90% at the thickness of 100 nm/200 nm/100 nm, which is superior to that of LiTaO₃ at the same thickness. The structure of ATA electrolyte was optimized with the optical constants of LiAlOₓ and Ta₂O₅ via software of Essential Macleod in Fig. 2(e), which shows the relationship between the luminous transmittance of ATA electrolyte and the film thickness of top and bottom LiAlOₓ layer, that is, “LiAlOₓ (bottom layer, thickness t₁)/Ta₂O₅ (200 nm)/ LiAlOₓ (top layer, thickness t₂)”. When t₁=t₂=0, namely only Ta₂O₅ monolayer, the visible light transmittance corresponds to the lowest trough. When the top and bottom layer of LiAlOₓ was introduced, the visible light transmittance increases in a wavy manner and reaches the maximum value over 90% under certain conditions (t₁=t₂=100 nm). Additionally, the designed structure was calculated according to the transparent state of Ta₂O₅ when lithium ions locate on the side of electrochromic layer under electric field. Therefore, LiTaO₃ (LTO) is equivalent to Ta₂O₅ (TO), which has little difference in optical constants without lithium ions.

2.4 Electrochemical property of the ATA based ECDs

As shown in Fig. 4(a), by means of optical design, the optical transmittance of the sandwich structured electrolyte (ATA) has been greatly improved on the premise that the ionic conductivity is not lower than that of LiTaO₃ at the same thickness. The designed ATA based ECDs have satisfactory coloring efficiency of 79.6 cm²/C while changing color reversibly (Fig. 4(b)). The inset of Fig. 4(b) reflects reversible color change between the bleached and colored states of the as-prepared ECD with the size of 20 mm×20 mm. Moreover, its response time for coloring and bleaching is as short as 1.9 and 1.6 s, respectively (Fig. 4(c)), which is mainly due to the convenient transport channels and rich ion reservation of ATA sandwich structured electrolyte. At the meantime, it keeps stable optical modulation after 200 cycles with in-situ testing units fixed wavelength at 630 nm (Fig. 4(d)).

### Table 2  Comparison of sputtering efficiency for several typical systems

| Layer       | Target   | Power supply | Power density/(W·cm⁻²) | Sputtering rate/(nm·min⁻¹) | Sputtering efficiency/(nm·min⁻¹)/(W·cm⁻²) | Ref.       |
|-------------|----------|--------------|------------------------|---------------------------|------------------------------------------|-----------|
| Ta₂O₅       | Ta₂O₅    | RF           | 0.57                   | 2.7                       | 4.74                                     | [23]      |
| Ta₂O₅       | Ta        | DC           | 0.89                   | 15                        | 16.85                                    | This work |
| LiTaO₃      | LiTaO₃   | RF           | 0.48                   | 1.2                       | 2.50                                     | [24]      |
| LiAlOₓ      | Li-Al    | DC           | 0.16                   | 1                         | 6.25                                     | This work |
| WO₃         | WO₃      | RF           | 1.78                   | 5                         | 2.81                                     | [25]      |
| NiO         | NiO      | RF           | 0.64                   | 3.6                       | 5.63                                     | [26]      |
| Ni          | Ni       | DC           | 0.32                   | 5                         | 15.63                                    | This work |
3 Conclusions

In summary, we have developed the sandwich structured electrolyte with high transparency of luminous transmittance over 90% and remarkable sputtering efficiency by DC reactive magnetron sputtering using alloy and metal target. Additionally, ATA sandwich structured electrolyte as the ion conducting layer has been introduced into a seven-layer all-solid-state ECD consisting of ITO/NiO/LiAlO$_x$/Ta$_2$O$_5$/LiAlO$_x$/WO$_3$/ITO. Furthermore, ATA-based ECDs realized satisfactory coloration efficiency of 79.6 cm$^2$/C, fast switching speed as short as 1.9 s for coloring and 1.6 s for bleaching, and excellent cycling stability over hundreds of cycles. Hence, ATA-based ECDs by optical design are expected to realize mass production and practical application in the near future.

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光学设计用于全固态电致变色器件的高溅射效率三明治结构电解质

贾汉祥1,2, 邵泽伟1,2, 黄爱彬1, 金平实1, 曹逊1
(1. 中国科学院 上海硅酸盐研究所，高性能陶瓷和超微结构国家重点实验室，上海 200050；2. 中国科学院大学，北京 100049)

摘要：全固态电致变色器件以其光学对比度高、响应速度快以及良好的循环稳定性等特点而广泛应用于节能窗、屏幕显示、多功能储能设备等诸多领域。然而，传统的基于单层电解质体系的全固态电致变色器件常受限于光学透过率和溅射效率的不足。本工作利用反应直流磁控溅射技术成功制备了基于LiAlOx/Ta2O5/LiAlOx(ATA)三明治结构电解质的全固态电致变色器件。通过引入ATA三明治结构电解质，所制得的七层体系电致变色器件(ITO/NiO/LiAlOx/Ta2O5/LiAlOx/WO3/ITO)兼具了优异的透光率和可观的溅射效率。该全固态电致变色器件取得了令人满意的着色效率(79.6 cm2/C)，更快的响应速度(着色时间1.9 s，褪色时间1.6 s)以及数百次循环的良好稳定性。此外，ATA三明治结构电解质充分利用了Ta2O5优异的离子传输速率和稳定性，并提供了足够的锂离子以满足快速变色切换的需求。因而，通过连续直流溅射制备的基于ATA三明治结构电解质的全固态电致变色器件有望为高性能电致变色器件的量产和实际应用提供重要的指导。

关键词：无机全固态；电致变色器件；多层电解质；溅射效率；光学设计

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