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SHORT COMMUNICATION

Anti-corrosive and charge-storage capabilities of ZrO_2 sputter coated over Al thin film

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சுருக்கம்:
ZrO_2 என்பது ஒரு சிறந்த மின்கடத்தா பொருள் ஆகும், மேலும் இது பல்வேறு பயன்பாடுகளில் பரந்த அளவில் பயன்படுகிறது. ZrO_2 பூச்சுகளின் இரட்டை செயல்பாடு, ஆன்டி-காரோசிவ் பூச்சுகளாகவும் ஆற்றல் சேமிப்பு பொருட்களாகவும் செயல்படும் திறன் மூலம், பொருள் அறிவியலில் புதிய வாய்ப்புகளை உருவாக்குகிறது. முந்தைய ஆய்வுகள் தனித்தனியாக ஆன்டி-காரோசிவ் திறன் அல்லது ஆற்றல் சேமிப்பு திறனை மையமாகக் கொண்டிருந்தாலும், இந்த ஆய்வு இந்த இரு பண்புகளையும் ஒருங்கிணைக்கும் வழிகளை ஆராய்கிறது. ஆய்வின் முடிவுகள் ஸ்பட்டர் டெபோசிஷன் முறையை மேம்படுத்துவதன் மூலம் இரட்டை செயல்பாட்டை வெளிப்படுத்துகின்றன. இந்த கண்டுபிடிப்பு ஒற்றை-செயல்பாட்டு பூச்சுகளின் குறைகளை சமாளிக்கிறது. மேலும், இது கடுமையான சூழல்களிலும் அதிக ஆற்றல் தேவைப்படும் சூழல்களிலும் பன்முக பயன்பாடுகளுக்கு வழி அமைக்கிறது. ஆய்வின் முடிவுகளின்படி, ZrO_2 பூச்சு அலுமினியத்தின் (Al) ஆன்டி-காரோசிவ் திறனை மேம்படுத்துகிறது; பூச்சு நேரம் அதிகரிக்கக்கூடிய அளவில் பாதுகாப்பு அதிகரிக்கிறது. மேலும், சைக்லிக் வோல்டாம்மெட்ரி மூலம் மேற்கொண்ட ஆற்றல் சேமிப்பு ஆராய்ச்சியில், மெல்லிய ZrO_2 பூச்சு குறைந்த தடிப்பிலேயே சிறந்த ஸ்பெசிபிக் கேபாசிடென்ஸ் அளிக்கிறது என்பதற்கான ஆதாரங்களை உறுதிப்படுத்துகிறது. ZrO_2 மெல்லிய படலத்தின் இரட்டை செயல்பாடுகளை உறுதிப்படுத்துவதுடன், பயன்பாடுகளின் அடிப்படையில் பூச்சின் தடிப்பை சரிசெய்வது அவசியம் என்பதை தெளிவுபடுத்துகிறது. எதிர்காலத்தில், பூச்சின் தடிப்பை முறைப்படுத்துவதன் மூலம், மின்முனையின் சார்ஜ் சேமிக்கும் திறனை ஆன்டி-காரோசிவ் செயல்பாடுடன் இணைத்து மேம்படுத்த முடியும். இதனால், இரு பண்புகளுக்கும் பாதிப்பு இல்லாமல் சாதனங்களை உருவாக்குவதற்கான உகந்த தீர்வை அடையலாம்.

Abstract:
ZrO_2 is an excellent dielectric material and is used in many applications. The dual functionality of ZrO_2 coatings as both anti-corrosive layers and energy storage materials presents a novel avenue in material science. While previous studies have focused individually on either corrosion resistance or energy-storage capabilities, this work explores the synergistic integration of these properties. The study demonstrated enhanced performance in both fields by optimizing the sputter deposition process. This approach addresses the limitations of single-function coatings and provides a pathway for multifunctional applications in harsh and energy-intensive environments. From the results, the ZrO_2 coating improves the corrosion resistance of Al as coating time increases; the protectiveness improves. Further, the charge storage analysis through cyclic voltammetry (CV) measurements supports the fact that the less thickness of the dielectric ZrO_2 improved specific capacitance. This study validated the dual function of ZrO_2 thin film, and thickness should be tuned as per the applications. In the future, optimizing the coating thickness can lead to an optimum value where the electrode displays charge-storing capability with corrosion resistance behavior without compromising both properties to a greater extent.

Keywords: zirconia, aluminum, coating, corrosion, charge storage, dual function

Introduction

Zirconia (ZrO_2) is a widely used material as it has high chemical stability at elevated temperatures. Therefore, ZrO_2 is used in many applications such as batteries, thermal protective coatings, and capacitor dielectrics (1–3). Thin aluminum (Al) films are utilized to fabricate microchips, solar energy production, and mobile phones. Al thin film is used owing to its high conductivity, lightweight composition, and ease of deposition during manufacturing. Despite its advantages, Al thin film faces challenges like corrosion, especially in harsh environments with high water or chemical content (4). The occurrence of corrosion in Al thin films leads to the deterioration of the device's performance. This can cause increased resistance towards conductivity, leading to device faults (5). Even though Al forms a thin layer of oxide over the surface, it doesn't provide long-term corrosion protection (6–8). As a chemically stable ceramic material, ZrO_2 is a potential coating material for enhancing corrosion resistance. Yang et al. (9) improved the corrosion resistance of Mg alloy through polydimethylsiloxane/ZrO_2 nanoparticles coating. Here, polydimethylsiloxane acted as a polymer matrix where the ZrO_2 nanoparticles improved the density of the matrix. In another study, Zhao et al. (10) improved the corrosion behavior of 316L stainless steel by coating ZrO_2 through a cathode plasma electrolytic deposition technique. Owing to the dense coating of ZrO_2, 316L stainless steel displayed enhanced anti-corrosive behavior in a 3.5 wt.% aqueous solution of NaCl. As a result, ZrO_2 is an effective material for improving the corrosion resistance behavior of Al thin films (11). ZrO_2 can work as a corrosion barrier, protecting Al from direct exposure to corrosive ions, and extending the substrate's durability. Furthermore, due to its remarkable dielectric properties, ZrO_2 is appropriate for usage in capacitors, sensors, and high-frequency devices (12). Especially, ZrO_2 is an exceptional material for charge storage because of its high dielectric constant and low dielectric loss. Raj et al. (13) prepared ZrO_2 nanoparticles, and its charge-storing capacity was evaluated as 246.98 Fg^{-1}. The charge-storing efficiency was 98% even after 3000 cycles of charging and discharging. Likewise, Mansoor et al. (14) prepared ZrO_2 solid-state sintering technique, and its electrochemical charge storage behavior was analyzed. The specific capacitance was found to be 546 Fg^{-1}. Further, coating a thin film of ZrO_2 poses challenges to material compatibility with the substrate, deposition techniques, uniformity, etc. Physical vapor deposition is a versatile technique where the thin film can be prepared with high quality, precise control, strong adhesion, etc., making it a better choice for depositing ZrO_2.

In this study, ZrO_2 thin film was sputter coated over Al-coated glass substrates. Even though ZrO_2 was used as an anti-corrosive and charge storage material, its multi-functional studies have not been reported so far. Further, the influence of coating thickness on its dual functionality is focused on the present work. The electrochemical workstation was used to assess the dual functionality of the ZrO_2 thin film as a corrosion-resistant and charge storage material. The results will provide insights into the potential applications of ZrO_2 coating.

Methodology

Preparation of Al thin film

Al thin film was prepared by the sputtering route (Model: 12″MSPT, Planar Magnetron RF/DC sputtering unit, Hind Hivac, India) over a glass substrate. Before carrying out Al deposition, the glass substrate was cleaned using chromic acid and ultrasonicated in water. Wiped with acetone and dried. Al target of size 2.0 in. diameter was developed using 99.99% Al powder through a pelletizer by applying a 50 kN load. The sputter coating was performed using direct current (DC) mode, and the coating time was fixed as 10 min with an applied voltage of 0.4 V. Initially, the pressure of the chamber was reduced to 10^{-6} mbar, and then by admitting Ar as a plasma-producing gas, the pressure was raised to 10^{-3} mbar. While switching on the DC power, the plasma was produced, resulting in the sputtering of Al atoms from the target and simultaneous deposition of Al on the pre-cleaned glass substrate fixed opposite to the Al target.

Coating of ZrO_2 thin film

For coating the ZrO_2 thin film over the Al substrate, the Al target was replaced with the ZrO_2 target. The procedure was repeated as in the case of Al sputtering. Here, the coating time was fixed as 20 min, 40 min, and 60 min. During the sputtering process, the ZrO_2 thin film was formed over the Al film. The mass of the active material coated over Al thin film is recorded as 0.14 mg, 0.27 mg, and 0.46 mg for 20 min, 40 min, and 60 min coated samples, respectively. Further, the coated specimens were heated at 200 °C in an inert atmosphere to improve the adherence of ZrO_2 over Al.

Corrosion-resistant studies using Tafel analysis

3.5 wt% NaCl was dissolved in 100 ml of distilled water and used as a corrosive medium. The working electrode (ZrO_2/Al), reference electrode (Ag/AgCl), and counter electrode (Pt) were immersed in the corrosive medium. Initially, open circuit potential was performed for 30 min to stabilize the working electrode in the electrolyte. Further, Tafel analysis was performed within the potential window of −1 V to 1 V where the corrosion potential (E_{corr}) and pitting corrosion potential (E_{pit}) values were elucidated (15).

Further, corrosion protection efficiencies of the coating were evaluated using the formula,

$$\eta\% = \left\lfloor 1 - i_{corr}/i'_{corr} \right\rfloor \times 100 \quad (1)$$

where, i_{corr}—current density of the coated specimen, i'_{corr}—current density of uncoated specimen.

Charge storage behavior using CV measurements

The charge-storing performances of the prepared ZrO_2/Al thin films were evaluated using CV measurements. Here, 3 electrode systems were used where 0.1 M sodium sulfate was used as an electrolyte, recorded in the potential window −0.3 V to 0.3 V at various scan rates from 5 mV to 200 mV. Further, the specific capacitance (C_{sp}) of the prepared electrode was calculated using the formula (16),

$$C_{sp} = \frac{\text{area under CV curve}}{\text{scan rate} \times \text{voltage window} \times \text{mass of the material}} \text{F/g} \quad (2)$$

Results and discussion

Figure 1 displays the XRD pattern of ZrO_2/Al (60 min) specimen; the XRD pattern displayed a wide band at 2θ = 24°, indicating an amorphous nature, which was attributed to the amorphous glass substrate. The diffraction peaks at 2θ = 38°, 45°, 65°, and 78.54°, respectively, which verified the existence of Al crystalline phases through JCPDS card no.04-0787 (17). From the XRD pattern, it was clear that the peaks corresponding to the ZrO_2 phase were not seen. This may be owing to the fact that the ZrO_2 film thickness was very low, where the high-intensity Al peaks diminish the low-intensity ZrO_2 peaks (18).

Figure 2 displays the SEM image of ZrO_2/Al (60 min) where the image was recorded at an accelerating voltage of 20 kV and a working distance of 12.5 mm. Captured at a magnification of 50,000×, the SEM image revealed intricate details of the film. From the topographical image, it is clear that the ZrO_2 was coated over the Al film in a particle aggregate manner where the particles are found to be near spherical-shaped structures with a scale range of 100–150 nm. Even though ZrO_2 was found as particle aggregates, they were found uniformly all over the coated area.

The corrosion behavior of Al thin film sputter coated with ZrO_2 for different time intervals like 20 min, 40 min, and 60 min was studied using Tafel analysis against a 3.5% NaCl corrosive medium (**Figure 3**). Here, the prepared samples, such as bare Al, ZrO_2/Al (20 min), ZrO_2/Al (40 min), and ZrO_2/Al (60 min) were used as the working electrode in a 3-electrode system (19).

The uncoated Al displayed an E_{corr} of −0.83 V and E_{pit} of −0.53 V, substantiating high corrosion and pitting occurrence. From the figure, it was clear that the corrosion inhibition of Al improved with increased coating duration of ZrO_2. An E_{corr} of −0.626 V and E_{pit} of −0.52 V were obtained for the sample after a 20 min ZrO_2 deposition. After a 40 min ZrO_2 deposition, there was a further improvement in anti-corrosion behavior, with the E_{corr} of −0.597 V and the E_{pit} of −0.426 V. The sample with a ZrO_2 deposition of 60 min showed an enhanced anti-corrosive nature where the E_{corr} was −0.5 V and E_{pit} was −0.41 V, demonstrating a significant increase in inhibition against corrosion. These results demonstrate how ZrO_2 coatings hinder the corrosion behavior of Al. As the

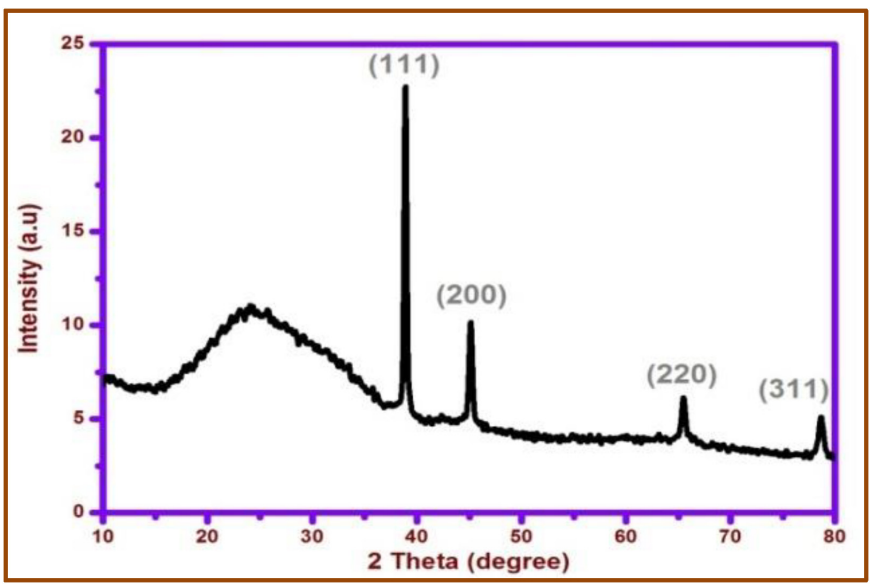

FIGURE 1 | X-ray diffracted pattern of ZrO_2/Al (60 min).

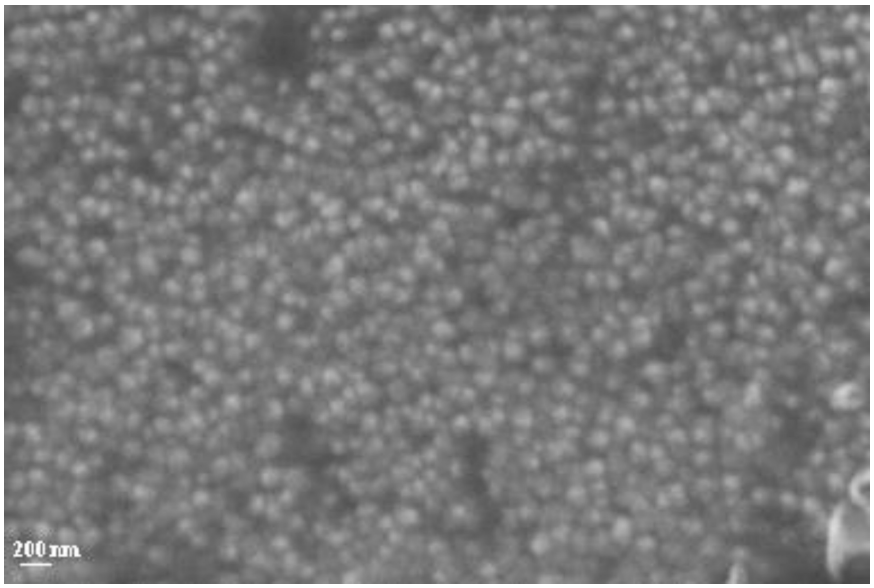

FIGURE 2 | SEM Analysis of ZrO_2/Al.

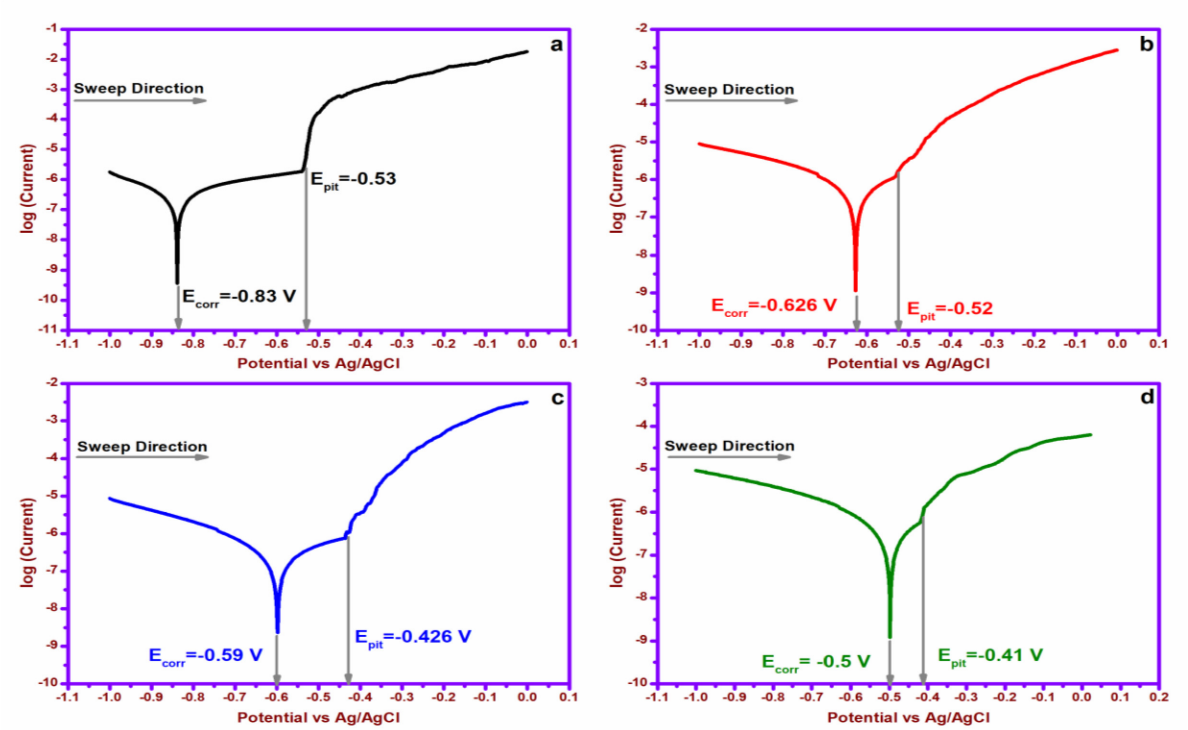

FIGURE 3 | Tafel analysis of **(a)** bare Al, **(b)** ZrO_2/Al (20 min), **(c)** ZrO_2/Al (40 min), and **(d)** ZrO_2/Al (60 min).

coating duration increases, ZrO_2 thickness increases, thereby effectively restricting the corrosive ions from reaching the underlying Al substrate (20).

ZrO_2 coatings are hard and can create a homogenous and inert thin film on the Al surface. This layer acts as a barrier that hinders the Al surface from corrosive ions. The ZrO_2 coating inhibits the electrochemical corrosion process by inhibiting corrosive ions from contacting the Al surface. ZrO_2 has good resistance to chemicals owing to its stability in acidic and mildly alkaline conditions. This characteristic allows the coating to remain intact and does not deteriorate when subjected to a corrosive environment; hence, it can preserve its protective efficacy over time.

Further, the corrosion protection efficiency (η%) of the prepared specimens was evaluated (21). η% were evaluated as 89%, 89%, and 92% for ZrO_2/Al (20 min), ZrO_2/Al (40 min), and ZrO_2/Al (60 min), respectively. These results

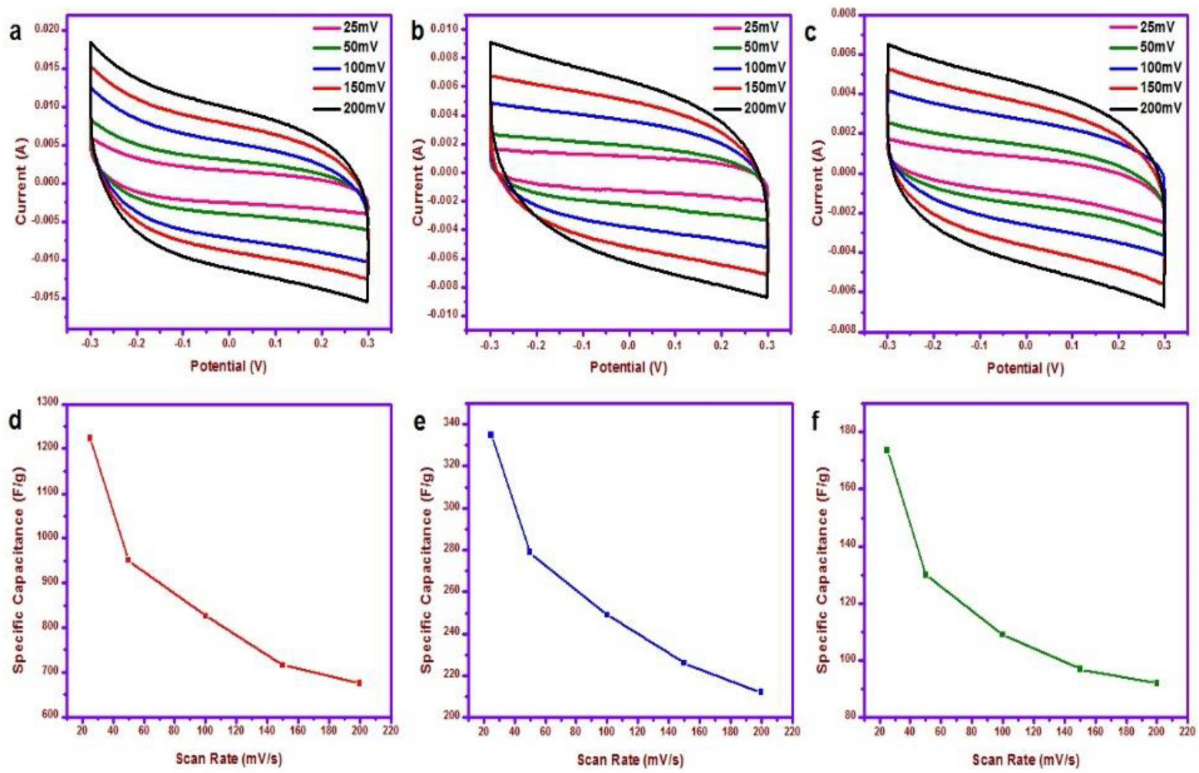

FIGURE 4 | CV and C_{sp} vs. scan rate plots of **(a, d)** ZrO_2/Al (20 min), **(b, e)** ZrO_2/Al (40 min), and **(c, f)** ZrO_2/Al (60 min).

also support the fact that the ZrO_2/Al (60 min) displayed better anti-corrosive behavior.

The supercapacitive behavior of ZrO_2 coated over Al film at various coating intervals was examined employing CV measurements utilizing CHI660new software. **Figure 4** displays the CV graphs of the prepared samples and their respective C_{sp} in F/g against 0.1 M Na_2SO_4 solution. Among various samples, the ZrO_2/Al (20 min) had higher C_{sp}, reaching 1223 F/g at a scan rate of 25 mV/s. The significant charge-storage capability demonstrated via the elevated C_{sp} was probably caused by the synergistic effect of ZrO_2 topography along with the large surface area that the 20 min ZrO_2 deposition created. Also, it is known that the reduction in the thickness of the dielectric material increases the C_{sp}. By comparison, ZrO_2/Al samples with 40 min and 60 min deposition time resulted in lower C_{sp} of 336 F/g and 174 F/g at 25 mV/s, respectively. As time increases, the ZrO_2 thickness increases, leading to low C_{sp}. The thicker and denser ZrO_2 dielectric layer in these samples may have blocked ion movement and reduced the available area for charge storage, which could explain the lower performance. This fact implies that the 20 min coating offers the highest combination regarding surface area, ionic availability, and electrolytic operation, which makes it the most promising candidate for high-performance charge storage electrodes. The C_{sp} declined as the rate of scanning increased, which is expected since a high scan rate restricts the number of ions that may diffuse into an electrode's substance (22). Since the ZrO_2 was coated using a physical vapor deposition route, which is well known for its coating stability and adherence. ZrO_2 coatings often demonstrate superior adherence to the Al substrate, guaranteeing the integrity of the coating despite mechanical stress or temperature variations due to the application of the physical vapor deposition method. This adherence reduces the likelihood of coating delamination, improving the overall performance of ZrO_2/Al thin films. Further, in settings characterized by mechanical wear, the exceptional hardness and abrasion resistance of ZrO_2 guarantee the efficacy of the protective layer. If the ZrO_2 coating is stable, then there will be a high cycling ability having a high retention rate.

Conclusion

The present study highlights the dual functioning of ZrO_2/Al thin films, exhibiting anticorrosive and supercapacitive characteristics. The results substantiated that the deposition time influences the performance, where the ZrO_2/Al (60 min) coating displayed improved anticorrosion efficacy and the ZrO_2/Al (20 min) coating exhibited the highest specific capacitance (1223 F/g). The findings indicate significant industrial potential for ZrO_2/Al coatings, especially in aerospace, automotive, and renewable energy sectors, where lightweight materials with integrated corrosion resistance and energy-storage capabilities are essential. Future studies

should concentrate on enhancing deposition techniques, such as roll-to-roll sputtering, to facilitate industrial manufacturing, while also assessing the long-term durability of these coatings under extreme environmental conditions, including elevated temperatures, salt, and fluctuating pH levels. This research was an attempt to tackle global issues in energy storage and material durability in advanced engineering fields.

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