Transparent Electrochemical Capacitors Developed Using RF-Sputtered Al-doped ZnO as a Structural Energy Storage to Replace Double-Glazed Window for a Smart Building

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ABSTRACT.

To achieve global decarbonization goals and the net-zero target, significant studies are essential for developing new electrode designs for energy storage that utilize environmentally abundant materials. In this work, we developed a transparent electrochemical capacitor (TEC) using aluminium-doped ZnO (AZO) film radiofrequency sputtered on ITO glass as a structural energy storage. We observed that the excellent electrical properties of the AZO film including carrier concentration of 6*.*54 × 1020 cm−3, Hall mobility of 25.8 cm2 V−1 s−1, and resistivity of 3.7 × 10−4 Ωcm contributed to electrochemical performances of the TEC. We measured the electrochemical properties of the TEC for both three-electrode and two-electrode measurement systems and found that the specific capacitance for a three-electrode study (liquid electrolyte) is 44.4 µF.cm-2 at 1 mV.s-1 in a and is 5.93 µF.cm-2 at 1 mV.s-1 in a two-electrode study (gel electrolyte). We observed that both the electrochemical double-layer capacitance formation and pseudo capacitance contributed to the charge storing in TEC and were measured through Dunn’s method. The double-glazed window shape of the TEC exhibits its promising potential for implementation as structural energy storage in smart buildings. We also demonstrated its performance under various temperatures (-10 to 30°C) and its integration capabilities with solar cells. The long-term aim of this TEC is to develop a structural element for smart buildings or autonomous electric vehicles.

INTRODUCTION

Structural energy storage is a revolutionary innovation that combines energy storage and load-bearing capacities, resulting in materials that are both functional and efficient. This technique has numerous advantages, including weight reduction, increased space economy, and increased efficiency, making it essential in the automotive, construction, electronics, and aerospace industries. Its advancement is fueled by the escalating demand forefficient transportation solutions, space-saving applications, and environmental friendly practices. Structural energy storage aligns with modern technological and environmental aims by improving resource usage, reducing carbon footprints, and fostering the development of advanced, energy-efficient infrastructure 1-3. To achieve a sustainable society, the development of a clean energy solution has critical importance and needs. For this the design of energy storage and energy-efficient sensing systems are combined and integrated within the structures are mandatory. Among different structural energy storages, transparent structural energy storage has wide potential in innovative applications in architecture, consumer electronics, and the automotive sector, allowing for energy storage to be seamlessly integrated into windows, screens, and surfaces4. Incorporating storing and sensing features in the double-glazing glasses in continental regions makes it into smart windows for smart buildings. The recent studies on a transparent energy storage device including batteries and supercapacitors/electrochemical capacitors reveal its potential implementation as a structural energy storage device for smart windows. Transparent electrochemical capacitors (TEC) are revolutionizing the energy storage sector, featuring exceptional performance alongside unique functionality [ref]. These devices tackle the advantages of standard supercapacitor quick charging, better power output, and extended lifespan while introducing the innovative trait of transparency. This blend of attributes opens up new opportunities for diverse applications, including wearable electronics, smart windows, and transparent displays.

The key components of transparent energy storage are transparent substrates, current collectors, active materials, and gel or solid electrolytes. Transparent substrates, such as flexible polymers (PET, PU, PI, and PDMS) as well as rigid glass and silicon wafers, are favoured for their stellar optical, electrical, and mechanical properties 5-8. Current collectors in TEC need to be both conductive and clear and for this indium tin oxide (ITO), graphene, carbon nanotubes (CNTs), and conductive polymers like PEDOT are received much attraction 5, 8-10 [ref-p]. Active electrode materials play a crucial role in determining the performance and transparency of supercapacitor. A variety of materials, including metal oxides, carbon materials, conductive polymers, and hybrid combinations, are commonly employed 8, 9 [ref-p]. Among these, metal oxides stand out for their high specific capacitance, chemical stability, and tunability, making them ideal for TEC applications. Their abundance and cost-effectiveness further enhance their appeal, offering a sustainable pathway towards scalable and eco-friendly supercapacitor technology. Among metal oxides, aluminum-doped zinc oxide (AZO) presents several advantages as an electrode, including high optical transparency (>90%), excellent electrical conductivity from aluminum doping, and compatibility with various electrolytes and flexible polymer substrates [ref]. Additionally, AZO is a cost-effective alternative to materials like ITO, making it suitable for large-area applications. Its transparency, conductivity, stability, and flexibility position AZO as an attractive electrode material for transparent supercapacitors. Electrolytes are selected based on criteria such as transparency, ion conductivity, and compatibility with electrode materials, ensuring optimal performance across diverse applications. Gel and solid electrolytes each offer distinct advantages; gel electrolytes provide enhanced mechanical flexibility and safety, while solid electrolytes offer superior mechanical strength, thermal stability, and effective ion transport 11-13.

In this work, we created a TEC using glass as a substrate, capable of storing energy and sensing temperature variations. This TEC can easily replace the place of double-glazing glasses to make the building smarter as schematically represented in Figure 1a and in which energy can also store from solar cell. We developed the TEC with AZO as an active electrode on an ITO current collector and glass substrate for transparent energy storage analysis. This electrode was evaluated separately on material and device aspects. AZO films have a polycrystalline hexagonal crystal structure, similar to undoped ZnO, as presented in Figure 1. Al doping can cause lattice distortions and defects in the ZnO crystal structure. The lattice parameters of AZO are somewhat less than those of undoped ZnO, indicating that Zn2+ ions are replaced with smaller Al3+ ions. The crystallinity and crystal size of AZO films decrease with increasing Al doping concentration, as greater doping levels introduce more flaws and disorder into the crystal structure14. Al atoms serve as substitutional impurities or dopants in the ZnO lattice, replacing certain Zn atoms. Al doping introduces free electrons into the ZnO lattice, which increases charge carrier concentration and electrical conductivity. While reacting with electrolyte, in AZO both electrochemical double layer capacitance (EDLC) and pseudo capacitance are generated for energy storage in TEC. The AZO electrode showed a specific capacitance of 44.4 µF.cm-2 at 1 mV.s-1 in a three-electrode study and 5.93 µF.cm-2 at 1 mV.s-1 in a two-electrode study as summarized in Figure 1b. The charge stored in the AZO device indicates a diffusion-controlled nature. Further to demonstrate its application as a structural energy storage we investigated the influences of -10 to 30 °C on the TEC and we found that in low temperatures the ion movement is slower, resulting in decreased electrochemical performance as given in Figure 1c. TEC could be potentially implemented for clean energy storage in smart buildings or sustainable energy autonomous system technologies.

A diagram of a solar panel

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Figure 1: (a) Schematic illustration of TEC based on AZO sputtered on ITO-coated glass with gel electrolyte acting as a double-glazed window for structural energy storage (b) variation of capacitance of the AZO in three-electrode and two-electrode study (c) the capacitance variation of TEC under various temperature.

**Results and Discussion**

**Material and Electrical Characterization:** XRD patterns of the AZO film coated on the ITO-coated glass are shown in Figure 2a. A distinct (002) peak is observed at a 2θ angle of 34.45°, indicating that the films were predominantly oriented along the c-axis and conform to the hexagonal crystal structure (ICDD-PDF # 00-036-1451). Figure 2b shows the SEM image of the deposited films, revealing densely packed grains of varying sizes on the surface. AFM analysis, shown in Figure 2c, indicates that the films have an average RMS roughness of 7 nm. The thickness of the AZO film, measured using spectral reflectance, was found to be 745±1 nm.A carrier concentration of 6*.*54 × 1020 cm−3, Hall mobility of 25.8 cm2 V−1 s−1 and resistivity of 3.7 × 10−4 Ωcm were measured for the AZO-coated film over the ITO thin film. The sheet resistance estimated was 5 Ω/

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Figure 2: (a) XRD pattern (b) SEM image (c) AFM) image of the AZO film coated over the ITO film

**Electrochemical Characterization**

***Three Electrode Measurement:*** A three-electrode system is used to evaluate the electrochemical performance of TEC electrode materials. Figure 3a shows a quasi-rectangle shape of the cyclic voltammetry (CV) curve which represents the presence of both electrochemical double-layer capacitance (EDLC) and pseudo capacitance mechanism in the TEC electrode. Additionally, the CV curve's mirror-image shape confirms the reversible nature of the ion transfer and redox reaction occurring at the electrode surface. This indicates that the AZO electrode can hold ions on the surface and within the inner layers of the wurtzite structure of the AZO. The wurtzite structure of AZO contains large channels and interstitial sites that facilitate ion diffusion, resulting in decreased diffusion paths and high ion mobility, which is critical for achieving fast charge and discharge rates 15-17. Doping Al with ZnO ions typically involves replacing some of the Zn ions sites with Al ions. This introduces more free electrons (n-type doping), which improves electrical conductivity and enhances ionic characteristics. Aluminium doping enhances ZnO's electronic conductivity, which benefits ion movement by lowering internal resistance in electrodes. Al doping can generate oxygen vacancies and zinc interstitials, which can act as channels or locations for ion transport. These defects can aid in the diffusion of ions. This can increase the TEC's overall efficiency18-20.

The high conductivity of the prepared AZO film leads to form an EDLC on the surface of the electrode. Hence both EDLC and pseudo capacitance reactions contributed to enhancing the capacitance of the TEC electrode. This is evaluated by measuring the surface (Qs) and diffusive (Qd) charge storage phenomena from the CV curves of the AZO film. The linear fit between the scan rate and peak current in Figure S1 shows a slope of 0.45, indicating a diffusion-controlled reaction in AZO electrodes concerning Ag|AgCl and platinum. The value of Qs is primarily due to the charge generated at the electrode-electrolyte interface and, due to the rapid charge transfer kinetics, it is regarded as EDLC. The value of Qs is calculated as the intercept of Qt vs. the inverse square root of the scan rate, as shown in Figure 3b. The Qd results from redox reactions of electrodes in the bulk material, which have slower kinetics and are inversely proportional to the square root of the scan rate. Based on this Qd and Qs the Qt of the TEC were measured and is given in Figure 3c. It was observed a high value of Qt for a lower scan rate is showing 50.3 µC cm-2 at 1 mV s-1. This suggests both diffusion-controlled and capacitive contributions to charge storage in TEC electrodes. The percentage of contribution from Qs and Qd for lower scan rates is given in Figure 3d. It was found that Qd's contribution is significantly higher at low scan rates compared to Qs. As an example, the variation of Qs and Qd in the CV curve is shown in Figure 3e at 10 mV.s-1. Due to the fast movement of ions in a high scan rate, the Qd decreases with the scan rate as shown in Figure 3d. Hence due to both these contributions, the AZO film exhibits excellent specific capacitance (Csp) of 44.4 µF.cm-2 at a very low scan rate of 1 mV.s-1. In addition, Csp at different scan rates shows a decrease with increasing scan rates, as depicted in Figure 3f. At lower scan rates, the velocity of ion movement is reduced, providing more time for ions to penetrate the porous structure, resulting in higher Csp and Qd.

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Figure 3: Three electrode study data a) CV at different scan rates. b) Qt V/s inverse square root of the scan rate. c) Qt at different scan rates d) contribution per cent of Qs and Qd. e) Variation of Qs and Qd in CV plot at 10mV.s-1. f) Csp at different scan rates.

From the CV curve, the ECSA of the AZO electrode is also measured and is found to be 455 mm2. For this, the of Cdl was calculated measured from the slope of a linear regression between current density differences (∆j/2 = (ja-jc)/2) in the middle of the potential window of CV curves and scan rates as shown in Figure S2a and S2b. The energy density (ED) of the AZO film was measured and was found 2.2 nWh cm-2 at 1 mV s-1, and its variation with different scan rates is shown in Figure S3.

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Figure 4: Three electrode study data a) GCD at different current densities. b) Csp at different current densities. c) ED and PD at different current densities. d) Nyquist plot (inset shows high-frequency region). e) Bode impedance f) Bode phase angle

The electrochemical properties of the AZO electrodes were further investigated by conducting GCD measurements at different current densities, as shown in Figure 4a. The GCD curves also confirm the reversibility of the electrode materials during the charging/discharging process. Due to pseudocapacitive behavior, the GCD curve distorted from a symmetric triangle at the lowest current densities. The device exhibited insignificant IRdrops in the GCD curve at various current densities, indicating low internal resistance. This low resistance facilitates the rapid movement of ions, leading to good power density. At a current density of 0.26 µA.cm-2, the device showed a Csp of 15.7 µF.cm-2, and the variation of Csp at different current densities is shown in Figure 4b. For the same current density, the ED and power density (PD) are observed at 0.78 nWh.cm-2 and 0.08 µW.cm-2, respectively. The variation of ED and PD with current density is illustrated in Figure 4c.

Furthermore, the frequency response was analyzed using electrochemical impedance spectroscopic (EIS) analysis. The Nyquist plot in Figure 4d shows the real and imaginary impedance of the electrode, with an overall real impedance of 210.2 Ω and an imaginary impedance of 1325.58 Ω. The lower frequency region of the Nyquist plot displays a characteristic straight line with a slope, indicating diffusion-controlled Warburg impedance and the presence of an electric double layer at the electrode-electrolyte interfaces. The capacitive behaviour of the electrode is further confirmed by the Bode phase angle and impedance plot analysis, as shown in Figures 4e and 4f. The Bode impedance decreases with increasing frequency (depicted in Figure 4e), indicating the capacitive nature of the electrode. At 1 mHz, the phase angle (shown in Figure 4f) for the AZO electrode reached a maximum of almost −90°, similar to that of an ideal capacitor. The relaxation time constant (τ0) distinguishes between resistive and capacitive behaviors, defining the merit of an electrochemical device. A low τ0 value suggests a high-power performance, supporting the electrochemical capacitive feature. The value of τ0 is commonly derived using τ0 = 1/f0, where the projected phase angle is 45°, indicating equal capacitive and resistive impedances. The Bode plot showed a time constant of 4.6 ms for the AZO electrode. This short relaxation time indicates that the device charges and discharges quickly.

***Full Cell Characterization***: The two-electrode system offers simplicity and can measure the overall behavior of the AZO TEC device. Figure 5a shows the CV of the two-electrode study of the AZO device, which has a similar shape to that in the three-electrode configuration and indicates the presence of EDLC and pseudo capacitance. This suggests that ions can be stored on the surface and within the crystal structure. This is verified by calculating diffusion-controlled and capacitive-controlled charge storage contributions. The Qt values for different scan rates are presented in Figure 5b, showing 7.12 µC.cm-2 at 1 mV s-1, and their contributions from both Qd and Qs are illustrated in Figure 5c. The value of Qs is calculated as the intercept of Qt vs. the inverse square root of the scan rate, as shown in Figure S4. It shows that Qd is greater than Qs at lower scan rates because the slower ion movement allows enough time for penetration into the core of the AZO material. Compared to the three-electrode configuration, ion movement is slower here due to the gel electrolyte, resulting in a 24% decrease in Qd in the two-electrode study. The variation in Qs and Qd in the CV curve is shown in Figure 5d at 1 mV.s-1. The linear fit between the scan rate and peak current is shown in Figure S5 and it has a slope of 0.58, indicating a diffusion-controlled reaction in AZO electrodes.

The two-electrode assembly showed a Csp of 5.93 µF.cm-2 at 1 mV.s-1, which decreased with increased scan rates as shown in Figure 5e. This is due to the increased velocity at higher scan rates, leading to reduced utilization of inner voids in the electrodes. The reduction in the Csp of the two-electrode system compared to the three-electrode system is mainly due to several factors. The three-electrode system typically uses a reference electrode that provides a more controlled measurement environment, reducing the distance and resistance ions face. In a two-electrode setup, both electrodes are polarised, unlike the isolated working electrode in a three-electrode setup. Additionally, the combined resistance of both electrodes is higher in a two-electrode system, reducing charge storage efficiency. Gel electrolytes used in two-electrode setups delay ion movement more than liquid electrolytes in three-electrode systems [7-9]. The ED at different scan rates is shown in Figure 5f, displaying 0.29 nWh.cm-2 for a lower scan rate.

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Figure 5. Two electrode study data a) CV at different scan rates. b) Qt at different scan rates. c) contribution in % of Qs and Qd. d) Variation of Qs and Qd in CV plot. e) Csp at different scan rates. f) Energy density at different scan rates.

The electrochemical properties of the TEC were further examined through GCD measurements at various current densities, as depicted in Figure 6a. The nature of the GCD curve is similar to the 3-electrode study. Due to the combination of EDLC and pseudocapacitive behaviour, the GCD curve distorted from a symmetric triangle at the lowest current densities. At a current density of 0.26 µA cm-2, the device showed a Csp of 10.5 µF.cm-2, and its variation with current densities is shown in Figure 6b. The ED and PD are approximately 0.52 nWh.cm-2 and 0.08 µW.cm-2, respectively, across different current densities.

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Figure 6. Two electrode study data a) GCD at different current densities. b) Csp at different current densities. c) Ed and PD at different current densities. d) Nyquist plot. e) Bode impedance and phase angle.

Moreover, the frequency response was analyzed using EIS. The Nyquist plot in Figure 6d displays both real and imaginary impedance of the electrode, approximately within the range of 150 kΩ. This high impedance arises from various factors including (i) gel electrolytes exhibit higher ionic resistance compared to liquid counterparts (ii) both electrodes contribute to impedance due to polarisation effects (iii) the semi-solid nature of gel electrolytes hampers ion transport (iv) their's increased contact resistance between the gel electrolyte and electrodes and (v) thicker gel layers elongate ion transport paths 21-24. The lower frequency region of the Nyquist plot exhibits a characteristic straight line with a slope, indicating diffusion-controlled Warburg impedance and the presence of an electric double layer at the electrode-electrolyte interfaces. The capacitive behaviour of the electrode is further confirmed by the Bode phase angle and impedance plot analysis, as depicted in Figures 6e and 6f. The Bode impedance diminishes (Figure 6e) with increasing frequency, signifying the capacitive nature of the electrode. At 1 mHz, the phase angle for the TEC nearly reached -80°, akin to an ideal capacitor. The Bode plot reveals a time constant of 2 ms for the TEC, indicating rapid charge and discharge capabilities.

In addition, to analyse the durability and longevity of the device repeated charging and discharging were carried out. This demonstrates that the AZO device is capable of retaining 75% of its capacity after 1000 cycles. The capacity retention plot is displayed in Figure 7a. Figure 7b illustrates the growth of impedance over the long cycle life. It is evident from this plot that impedance increases with cycles, resulting in a capacity reduction for the device. Figure 7c presents the charging and discharging curves at various cycling intervals. Long cycle life is crucial for assessing the practical viability and lifetime of the material or device for its intended application. The electrochemical properties were also evaluated for a second device, which exhibited a similar nature to the first device. Figure S6a displays the GCD of device 2, following a pattern similar to device 1. A comparison of the specific capacitance and the charging-discharging curve at 1.06 µA.cm-2 for devices 1 and 2 is presented in Figures 7d and Figure S6b. The Nyquist plot (given Figure 7e) of both devices showed negligible variation in impedance. Figure 7f illustrates the Bode impedance and Bode phase angle of device 2, exhibiting a trend similar to device 1.

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Figure 7.a). The capacity retention of the device, b). EIS growth in between cycling, c). Charge-discharge curve at different cycles. d). Repeatability of specific capacitance forms GCD of TEC, e). Repeatability of Nyquist plot of TEC and f). Repeatability of bode plot of TEC

***Application of TEC as Smart Window***

TEC devices can store energy and sense temperature variations in their surroundings. The variation in the electrochemical performance is directly proportional to the variation in temperature. The variation in the ionic conductivity of the gel electrolyte in the TEC device leads to changes in its electrochemical performance under different temperatures. At higher room temperatures (e.g., 20 to 30°C), ions gain more energy, move faster, and increase ionic conductivity. However, at lower room temperatures (e.g., -10 to -20°C), ion movement is slower, resulting in decreased electrochemical performance. A schematic representation of ions movement in various temperature ranges is shown in Figures 8a to 8b. These changes in performance indicate a particular temperature around the device. Double-glazed windows in continental regions can be replaced with TEC devices as smart windows. TEC smart windows can store electrical energy and act as temperature sensors. The variation in the electrochemical performance of the TEC device was evaluated from -10°C to 30°C using an ESPEC constant climate chamber (LU114). The CV at different temperatures is shown in Figure 8c, clearly demonstrating variation with temperature. Figure 8d shows the specific Csp at different temperatures. At -10°C, the TEC has a Csp of 7.8 µF.cm². As the temperature increases, so does the Csp. This increase is due to the enhanced ionic conductivity of the gel electrolyte, which reduces impedance. The variation of impedance at different temperatures is shown in Figure 8e, revealing that the real and imaginary part of impedance decreases with rising temperature due to increased ionic conductivity. The bode plot shown in Figure 8f reveals the variation of the total impedance of the TEC at different temperatures and shows that an increase in temperature from -10 to 30 degrees resulted in a decrease in the impedance of the TEC.

The operating temperature of the TEC highly influences the electrolyte properties, including ionic conductivity, thermal stability, viscosity and solubility of the salt in the solvents25-28. The increase in temperature changes the thermo-physical properties and decomposition of electrolytes29. It has been reported previously that the ionic conductivity and mobility of ions will increase with increasing temperature29, and this fact is confirmed in our electrochemical analysis as well. This variation is also reflected in the capacitance and reactance of the TEC. In this work, we noted that decreasing temperature implies an increase in the value of impedance (Figure 8f) while the capacitance decreases (shown in Figure 8d). This could be due to the increase in resistance of the electrolyte with decreasing temperature. Also, the increase in capacitance with temperature could be attributed to the involvement of more ions triggered as a result of higher mobility of ions at higher temperatures, as shown in Figures 8(a) to 8(b). As compared to charging of SC at ambient temperature, the charging at lower and higher temperatures causes storing of a lesser or higher number of ions in porous structure (shown in Figure 8(a) to 8(b)), respectively. This structural energy storage device reduces the space required in buildings and houses. Additionally, we integrated the TEC with a 5V commercial solar panel (Sanyo Amorphous Solar Cell) to charge the device, as shown in the supporting video (SV1). This integration makes buildings smarter by enabling them to store energy within the structure and act as sensors without relying on non-renewable energy sources as represented in Figure 8g.

A diagram of different types of electrical components

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Figure 8: (a) and (b) Schematic of ion storing mechanism for low and high temperature for the TEC. (c) CV at different temperatures, (d). variation of Csp at different temperatures, (e) and (f). Nyquist and Bode plot at different temperatures and (g) integration of TEC with PV cell.

**Conclusion**

In this work, we studied the energy storage performances of RF-sputtered Al-doped ZnO (AZO) on ITO glass substrate. Based on this film we developed a transparent electrochemical capacitor (TEC) that acts as a structural energy storage. As an initial study, we measured the electrical properties of the AZO film including carrier concentration, Hall mobility, and resistivity, which is found to be 6*.*54 × 1020 cm−3, 25.8 cm2 V−1 s−1, and 3.7 × 10−4 Ωcm respectively. The superior electrical performances of this AZO film significantly enhanced the electrochemical performances of the TEC. The electrochemical studies shows that AZO electrodes can hold ions on the surface and within the inner layers of the wurtzite structure of the AZO. The wurtzite structure of AZO contains large channels and interstitial sites that facilitate ion diffusion, resulting in shortened diffusion paths and increased ion mobility, both of which are essential for achieving rapid charge and discharge rates. Our observations indicated that both electrochemical double-layer capacitance and pseudocapacitance contribution lead to charge storing in the AZO. The developed AZO-based electrodes demonstrated promising electrochemical performance, achieving a specific capacitance of 88.8 µF.cm-2 and 5.93 µF.cm-2 at 1 mV.s-1 in three-electrode and two-electrode studies, respectively. The device exhibited good practical viability and lifetime of the device with about 75% capacity retention after 10000 cycles. When Integrated into smart buildings, TEC at different temperatures shows that an increase in temperature from -10 to 30° resulted in a decrease in the impedance of the TEC. The developed TEC is poised to revolutionize the energy storage field by combining rapidcharging capabilities, high power output, and a long operational lifespan with the unique feature of transparency. This makes them excellent for use in smart windows, and transparent displays. By integrating TEC into smart windows, buildings can enhance their energy storage capabilities and improve operational sensing, thereby contributing to smarter architectural solutions.

**Experimental Section**

**AZO film development:** AZO film was coated onto an ITO-coated glass substrate (sheet resistance – ≤10Ω/□ and thickness – 180±3nm,Zhuhai Kaivo Optoelectronic Technology Co., Ltd. China) by radio frequency (RF) sputtering. The sputtering process in confocal configuration employed a 2-inch ceramic target composed of ZnO: Al (98:2 wt.%) with 99.95% purity (Advantech Co. Ltd. Japan). Before coating, the ITO-coated substrate was cleaned using nitrogen flow. For sputtering, the chamber was evacuated to a base pressure below 5×10-6 mbar initially and introduced high pure Ar (99.999%) as sputtering gas with a flow rate of 20 sccm. The depositions were carried out at a working pressure of 9×10-3 mbar, with no substrate temperature. Before coating, the target was pre-sputtered for 5 min to remove contaminants from the target surface. The RF power for the deposition was fixed at 120W. The substrate-to-target distance used was 7 cm, and the substrate holder was rotated during the deposition to obtain homogeneous films. The coated films were heat treated at 500°C in a reduced atmosphere (95% N2 and 5% H2) for 30 minutes to improve their electrical properties.

**Transparent electrochemical capacitor (TEC) Fabrication**: The glass substrate, coated with both AZO and ITO, serves as the electrode. The ITO functions as a current collector, while the AZO acts as an active material. The ITO portion is covered with an insulating paste (JE Solution.) to prevent any influence from the electrochemical reaction. After printing the insulative paste, the electrodes were heated in an oven at 80°C for 30 min. As the next step, a conducting wire is attached to the ITO side using silver paste (JE Solution) and heat treated in the oven at 80°C for 30 min. After the electrode fabrication, the AZO electrodes are sandwiched together in between gel electrolytes to assemble the electrochemical device. The electrode fabrication is shown in Figure 9a. For the TEC, the gel electrolyte is prepared by dissolving 10M LiCl (Sigma Aldrich-213233) in a 20 wt% polyvinyl alcohol (PVA) (Sigma Aldrich-363073) aqueous solution. LiCl possesses good ionic conductivity and thermal stability, a low melting point which makes it easier to process and incorporate into a gel and solid-state electrolytes and Compatibility with various electrode materials. PVA shows outstanding film-forming ability, high water solubility, chemical stability, mechanical characteristics, high ionic conductivity, thermal stability, and biocompatibility making it suitable for gel electrolytes. This gel electrolyte is then applied on top of the active material and left to dry in an air oven at 80 °C for 30 min. The schematic representation of the device is shown in Figure 9b. The transparency of the AZO electrode and the full device, TEC are shown in Figures 9c and 9d.

A diagram of a structure

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Figure 9. a). TEC electrode fabrication, b). Cross section of TEC, c). Transparency of TEC electrode and d). Transparency of TEC device.

**Characterisation**

**Material Characterisation:** Structural studies of the films were carried out by grazing incidence X-ray diffractometer (XRD) with CuKα radiation. (Rigaku Ultima IV, Japan). The surface morphology and roughness were examined by a Field Emission Scanning Electron Microscope (SEM) (Zeiss Sigma 300, Germany) at 1.5 kV and an Atomic Force Microscope (AFM) (Nanosurf Flex, Switzerland). The thickness of the films was estimated using an MProbe thickness monitor (SemiconSoft, USA).

**Electrical and Optical Properties**: The n-type behaviour and electrical properties such as resistivity, carrier concentration and mobility of AZO films were investigated by the Hall Effect measurement technique in van der Pauw configuration (ECOPIA HMS 3000) with 0.54T magnetic field. Transmittance spectra of AZO films were obtained using a UV/VIS spectrometer (Perkin Elmer Lamda 35).

**Electrochemical Characterisation:** Here we carried out both three-electrode and two-electrode measurements for the electrochemical characterisation by using Ivium soft (IviumStat2.h- Ivium Technologies B.V.). For a three-electrode analysis**, t**he AZO electrode is used as the working electrode, platinum (Metrohm) is used as the counter and Ag|AgCl|KCl (Ossila C2015B1) is used as the reference electrode in 10M LiCl in an aqueous solution. The two-electrode analysis was carried out for the full cell as-fabricated (Figure 1b). Techniques like Cyclic voltammetry (CV) Galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The CV carried from a small scan rate of 1 mV. s-1 to a higher scan rate of 200 mV. s-1 from 0 to 0.6 V. The GCD was carried out at different current densities from 0.26 to 5.3 µA. cm-2 from 0 to 0.6 V. The frequency response of the device is taken from 10 mHz to 1MHz for EIS analysis. The performances of the TEC including specific capacitance, energy density and power density were measured using the expression as given in supporting information. To determine the electrochemical properties of the device, the data was analysed from the electro-chemical characterisation technique by using the below equations. The electrochemical active surface area (ECSA) of an electrode is highly significant for enhancing energy storage and here it is calculated from the double-layer capacitance using the equation ECSA= Cdl/Cs, where Cdl is double-layer capacitance and Cs stands for the sample's specific capacitance or the capacitance of an atomically smooth planar surface of the material per unit area under the same electrolyte conditions. Although the smooth and planar surface of the electrode is important for measuring Cs and ECSA, the printed film does not have a smooth surface. Nevertheless, specific capacitances have been calculated for a variety of metal electrodes in acidic and alkaline solutions, with typical values ranging from Cs = 0.015-0.110 mF.cm-2 in H2SO4 to Cs = 0.022-0.130 mF.cm-2 in NaOH and KOH 30. Here, we consider the Cs value of 0.022 mF.cm-2. The value of Cdl was calculated by analysing the slope of a linear regression between current density differences (∆j/2 = (ja-jc)/2) in the middle of the potential window of CV curves and scan rates. The capacitive contribution in the electrode is calculated by using Dunn’s method.

Here the Qt expressed as

------- Eqn. 1

Here Qd is inversely proportional to the square root of the scan rate and hence

------- Eqn. 2

The Qt could be measured using the following equation.

------- Eqn. 3

The charge-storing mechanism of the device is analysed by linear fitting between the scan rate vs peak current (plotted in logarithmic scale). If the slope is 1 it is the expected capacitive charge contribution and for 0.5 or less it is the expected diffusion-controlled reaction 4.

ASSOCIATED CONTENT

**Supporting Information**.

The supporting information provided the method for evaluation of electrochemical properties of the TEC and few characterization graphs.

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