In situ synthesis of reduced graphene oxide/(Mg1-xZnx)TiO3 nanocomposites with excellent cyclic stability for supercapacitor electrode

P2MI STEI ITB 2026

Syadza Aisyah Hermadianti[1], Murni Handayani, Isa Anshori[2], Lok Kumar Shrestha, Fariz Irkham Muadhif[1], Muhammad Aulia Anggoro[1], Gagus Ketut Sunnardianto, Katsuhiko Ariga, Bambang Wisnu Widagdo, Frida Ulfah Ermawati, Arie Wibowo

[1] Magister Teknologi Nano, SPITM, ITB

[2] KK Teknik Biomedika, STEI, ITB

Abstract

To enhance the electrochemical performance and structural stability of supercapacitor electrodes, Zn^{2+}-doped reduced graphene oxide/magnesium titanate nanocomposites, rGO/$Mg_{1-x}Zn_xTiO_3$ (x = 0.05, 0.10, 0.15), were synthesized via liquid mixing followed by in-situ rGO growth. Characterization confirmed a dominant $MgTiO_3$ substitutional solid solution phase (70.77-99.99 wt%) coated with interconnected rGO nanosheets that expand surface area and accelerate charge transport. Among the tested compositions, the optimized rGO/$Mg_{0.90}Zn_{0.10}TiO_3$(rGO/MZ10T) electrode achieved a high specific capacitance of 437.96 F g^{-1} at 0.5 A g^{-1} and retained 99.1% of its capacitance after 5,000 cycles, demonstrating strong potential for durable, next-generation supercapacitors.

Keyword: Electrode materials, $MgTiO_3$, Supercapacitor.

Introduction

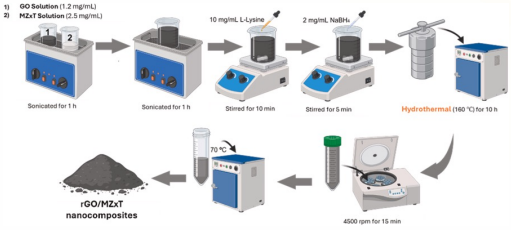
As global energy demand continues to rise, the transition toward renewable energy sources requires efficient and sustainable energy storage technologies. Supercapacitors have emerged as promising candidates to bridge the performance gap between conventional capacitors and batteries due to their rapid charge–discharge rates, high power density, and exceptional cycle life. To maximize both power transfer and energy capacity, hybrid supercapacitors combine electrostatic electrical double-layer capacitance (EDLC) from conductive carbon materials like reduced graphene oxide (rGO) with Faradaic pseudocapacitance from redox-active ceramics.

In this work, we develop an in situ synthesized nanocomposite combining rGO with Zn^{2+}-doped magnesium titanate, $(Mg_{1-x}Zn_x)TiO_3$, as a high-stability supercapacitor electrode. Incorporating Zn^{2+} ions into the $MgTiO^3$ crystal lattice preserves structural integrity and suppresses material degradation during cycling, while the interconnected rGO nanosheets provide a high-surface-area conductive network for rapid electron and ion transport. By systematically investigating the structural and electrochemical effects of Zn^{2+} doping, this study demonstrates a synergistic hybrid electrode capable of delivering high specific capacitance and long-term cyclic stability.

Research Method

The synthesis of pristine magnesium titanate ($MgTiO_3$, MT) and Zn^{2+}-doped $(Mg_{1-x}Zn_x)TiO_3$ (MZ_xT, where x = 0.05, 0.10, 0.15) was carried out via a liquid mixing route using high-purity Mg, Zn, and Ti metal powders dissolved in 12 M HCl. The mixed solutions were stirred and heated at 100—110 °C to form a white crust, which was ground into an amorphous powder and calcined at 800 °C for 2 hours to obtain crystalline precursors.

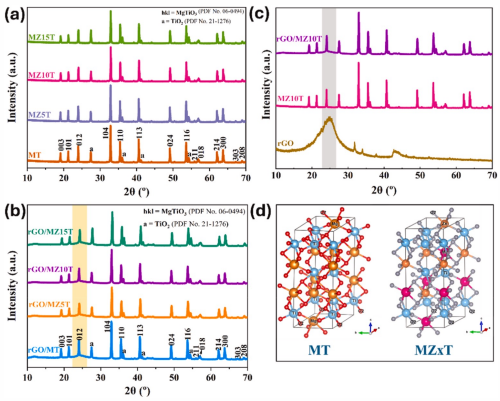
Subsequently, the rGO/MT and rGO/MZ_xT nanocomposites were prepared through an in situ hydrothermal method. Dispersions of graphene oxide and MT or MZxT powders were sonicated, combined with L-lysine and $NaBH_4$ as reducing agents, and heated in a Teflon-lined autoclave at 180 C for 10 hours before being centrifuged, washed, and dried at 70C.



Picture 1. Synthesis of nanocomposites prepared by in situ growth with the hydrothermal method.

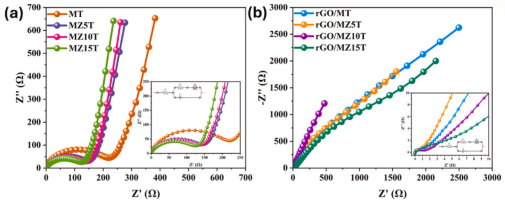
Discussion & Result

Structural, chemical, and morphological characterizations confirmed the successful synthesis of the $Mg_{1-x}Zn_xTiO_3$ solid solutions and their in situ integration with reduced graphene oxide. X-ray diffraction (XRD) and Rietveld refinement verified that rhombohedral $MgTiO_3$ remained the dominant phase (70.77–99.99 wt%) with a minor rutile TiO_2 secondary phase, while Zn^{2+} substitution into Mg^{2+} lattice sites systematically reduced the crystallite size from 51.15 nm to 48.95 nm without disrupting the crystal structure. X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray (EDX) mapping further corroborated the uniform incorporation of Zn^{2+} ions (evidenced by the Zn 2p peak at 1021 eV) alongside Mg, Ti, O, and C elements. Furthermore, FT-IR and Raman spectroscopy confirmed the in situ growth of rGO onto the ceramic surfaces via the presence of C=C, C–O, D, and G bands alongside Mg–O and Ti–O vibrations, while SEM and BET analyses revealed porous polygonal ceramic particles well-wrapped in interconnected rGO nanosheets, yielding a mesoporous network with an enlarged specific surface area of up to 42.15 m^2 g^{-1} for the rGO/MZ10T nanocomposite.

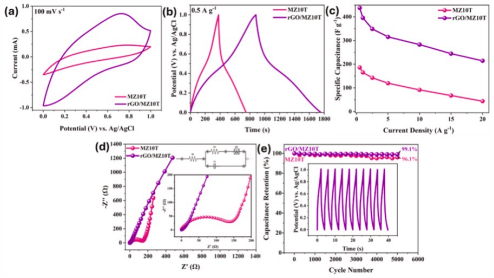


Picture 2. XRD patterns (a) MT, MZ5T, MZ10T, and MZ15T powders at 800 °C 2 h; (b) rGO/MT, rGO/MZ5T, rGO/MZ10T, and rGO/MZ15T based hydrothermal method; and (c) comparison of XRD patterns of the initial materials (rGO and MZ10T) with rGO/MZ10T nanocomposite. (d) Crystal structure of MT and MZxT (illustrated by VESTA software

Electrochemical evaluations demonstrated that the synergistic combination of Zn^{2+} doping and rGO integration significantly enhanced charge storage and transfer kinetics. In the three-electrode configuration, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) profiles revealed a hybrid charge-storage mechanism combining electrical double-layer capacitance (EDLC) from rGO with Faradaic pseudocapacitance from reversible Ti^{3+}/Ti^{4+} redox reactions and oxygen vacancies. Among all tested electrodes, the optimized rGO/$Mg_{0.90}Zn_{0.10}TiO_3$(rGO/MZ10T) achieved the highest specific capacitance of 437.96 F g^{-1} at a current density of 0.5 A g^{-1}, supported by reduced charge-transfer resistance (R_{ct}) in electrochemical impedance spectroscopy (EIS) and exceptional cyclic stability retaining 99.1% of its initial capacitance after 5000 cycles. Furthermore, when assembled into a symmetric two-electrode supercapacitor device, the rGO/MZ15T electrode delivered a specific capacitance of 14.7 F g^{-1} at 0.5 A g^{-1} alongside an energy density of 2.04 Wh kg^{-1} at a power density of 249 W kg^{-1}, confirming its practical viability for high-stability energy storage applications.



Picture 3. Nyquist plots of EIS analysis of the samples: (a) MT, MZ5T, MZ10T, MZ15T, and (b) rGO/MT, rGO/MZ5T, rGO/MZ10T, rGO/MZ15T composites.



Picture 4. Comparison of MZ10T and rGO/MZ10T materials: (a) CV curves at a scan rate of 100 mV s−1, (b) GCD curves at a current density of 0.5 Ag-1, (c) specific capacitance, (d) Nyquist plot, and (e) capacitance retention at 5000 cycles.

Conclusion

rGO/$Mg_{1-x}Zn_xTiO_3$ nanocomposites were successfully synthesized via a liquid-mixing route followed by in situ hydrothermal growth, confirming homogeneous Zn^{2+} doping and strong integration between the dominant $MgTiO_3$ phase and rGO nanosheets. The synergistic interaction between Zn^{2+} substitution and conductive rGO enhanced charge transfer, ion diffusion, and structural stability, enabling the optimized rGO/MZ10T electrode to achieve a high specific capacitance of 437.96 F g^{-1} with 99.1% capacitance retention after 5000 cycles, also with promising symmetric two-electrode device performance 2.04 Wh kg^{-1} energy density at 249 W kg^{-1} power density.