Controlled And Uniform Electrodeposition Of Manganese Dioxide On 3D Porous Scaffolds

Tech ID: 34813 / UC Case 2025-964-1

BACKGROUND

Depositing manganese dioxide (MnO_2) onto three-dimensional (3D) porous scaffolds—such as carbon lattices, nickel foam, or graphene frameworks—is a widely used strategy in developing high-performance electrochemical devices like supercapacitors, batteries, and catalysts.The primary objective is to build a hybrid structure that overcomes the natural material limitations of MnO_2 while maximizing its high energy storage capabilities. But conventional MnO_2 electrodeposition has a number of limitations.

Conventional MnO_2 electrodeposition tends to form thick coatings only on the outer surfaces of porous substrates. This excessive surface growth leads to pore blockage and poor penetration into the internal structure, impeding electrolyte access and reducing ion transport efficiency. This leads to low utilization of the available surface area and active material, severely limiting electrode performance.

Achieving both high mass loading and coating uniformity remains a major challenge. Existing methods such as hydrothermal synthesis often suffer from inherently low loading (typically < 40 mg cm-2), which constrains device energy density and practicality.

MnO_2 nucleation is dominated by random and large island growth, resulting in thick, non-uniform films with thickness gradients that hinder charge and ion transfer kinetics.

Highly loaded electrodes prepared by conventional methods exhibit thick MnO2 coating often show poor electrochemical kinetics due to poor electron/ion conductivity.

Finally, there is a lack of controlled interface regulation during electrodeposition.

TECHNOLOGY DESCRIPTION

The disclosed invention solves all of the above problems:

- enables a uniform MnO_2 film deposition in highly porous 3D scaffolds by regulating the electrode/electrolyte interfacial environments via redox mediation.
- enables the uniform deposition of an ultrahigh mass loading of MnO_2 (~ 240 mg cm^{-2}, 1600 mg cm^{-3}) in 3D porous structures.
- enables interface manipulation that promotes higher density, uniform and small-scale nucleation, yielding thin, dense and conformal MnO_2 films throughout the 3D scaffold that facilitate charge and ion

CONTACT

Jeff M. Jackson
jjackso6@ucsc.edu
tel: .



INVENTORS

- Chandrasekaran, Swetha
- Li, Yat
- Worsley, Marcus
- Xue, Xinzhe

OTHER INFORMATION

KEYWORDS

manganese dioxide, porous scaffold, 3D porous scaffold, MnO2, energy storage, electrodeposition, supercapacitor

CATEGORIZED AS

- **Materials & Chemicals**
  - Storage
  - Superconductors

RELATED CASES

2025-964-1

transfer kinetics.

▶ enables the formation of dense, ultra-thin, and uniform MnO_2 films with significantly reduced interfacial resistance, for example, decreasing MnO_2/3DGA interface resistance Rct1 from 5.26 to 2.71 Ohm and MnO_2/electrolyte interface resistance Rct2 from 10.85 to 8.18 Ohm, resulting in ultrahigh volumetric energy and power densities

▶ provides thermodynamic control over MnO_2 nucleation size and density, enabling reproducible, interface-controlled deposition with precise nucleation and morphological tuning. This strategy is also promising for extending to other critical materials such as high-k dielectric materials: zirconium dioxide (ZrO_2), aluminum oxide (Al_2O_3), hafnium oxide (HfO_2), and energy storage materials: hematite (Fe_2O_3), niobium pentoxide (Nb_2O_5).

Key elements of the method:

1. Preparation of Thermodynamically Engineered Electrolyte

An aqueous electrolyte is prepared by dissolving manganese sulfate ($MnSO_4$, 1M) as the Mn^{2+} source, followed by the addition of vanadyl sulfate ($VOSO_4$, 50 mM) to introduce the VO_2^+/VO^{2+} redox couple. This redox additive is critical for modifying the local thermodynamic environment at the deposition interface.

2. Electrodeposition Process Under Controlled Current

MnO_2 electrodeposition is conducted at a constant current of 40 mA cm^{-2}. The VO_2^+/VO^{2+} redox couple increases the overpotential and modifies the nucleation thermodynamics, leading to the formation of numerous small and uniformly distributed MnO_2 nuclei. These nuclei progressively coalesce into a thin, dense, and uniform MnO2 layer, conformally coating both the exterior and interior surfaces of the 3D porous scaffold.

Key Composition and Characteristics.

1. VO_2^+/VO^{2+} Thermodynamic Interface.

VO^{2+} modulates the local deposition thermodynamics, enabling small scale and uniform nucleation behavior of MnO_2. The VO_2^+/VO^{2+} redox pair has a standard potential lower than Mn^{2+}/MnO_2, ensuring that VO^{2+} is oxidized to VO_2^+ that further facilitates deposition uniformity. Meanwhile, VO^{2+} acts as a chemical redox mediator that reduces dead Mn^{3+} intermediates back to Mn^{2+} and suppresses Mn^{3+} hydrolysis, enabling uniform and fine MnO_2 deposition.

2. 3D Porous Scaffolds.

The scaffolds, such as 3D printed graphene aerogels (3DGA), provide high surface area, conductivity, mechanical robustness, and interconnected porosity for rapid ion transport. These structures are essential for hosting the conformal MnO_2 coating and enabling ultrahigh volumetric mass loading without clogging or pore collapse.

Functional characteristics

1. Achieved small MnO_2 nuclei exhibit a height of ~3.3 nm and radius of ~17 nm, compared to ~116 nm height and ~117 nm radius in conventional methods.

2. Shifting diffusion-controlled instantaneous nucleation to interface-controlled continuous nucleation mechanisms.

3. Achieved a record high MnO_2 mass loading (241 mg cm^{-2}, 1607 mg cm^{-3}) with a thin coating thickness of 3.5 μm on 3DGAs.

4. Reduced the interfacial charge transfer resistances: MnO_2/3DGA interface resistance Rct1 from 5.26 to 2.71 Ohm and MnO2/electrolyte interface resistance Rct2 from 10.85 to 8.18 Ohm.

5. Achieved a record high volumetric capacitance (106 F cm^{-3} for pseudo-capacitors, 140 mAh cm^{-3} for Zn//MnO_2 pouch cells), energy density (14.7 Wh L^{-1} for pseudo-capacitors, 189.7 Wh L^{-1} for Zn//MnO_2 pouch cells), and power density (97 W L^{-1} for pseudo-capacitors, 414.5 W L^{-1} for Zn//MnO_2 pouch cells), outperforming state-of-the-art thick electrode systems by 1 ~ 2 orders of magnitude.

6. Long-term stability is also demonstrated, with over 12,000 cycles in pseudo-capacitors and more than 200 cycles in Zn//MnO_2 batteries at ultra-high MnO_2 loading of 241 mg cm^{-2}.

APPLICATIONS

This invention demonstrates a novel interface thermodynamic engineering strategy for fabricating thick, conformal, high-performance MnO_2-based electrodes for energy storage.

ADVANTAGES

1. Thermodynamic Interface Control Enables Uniform Electrodeposition

Prior strategies to improve MnO_2 deposition on 3D substrates often rely on modifying the scaffold architecture, such as using 3D printed graphene aerogels (3DGAs) with graded channels or CNT networks. While these unique structures can enhance ion transport, they do not change the thermodynamics of MnO_2 nucleation and growth, which are important factors causing non-uniform coating. In contrast, by introducing a VO_2^+/VO^{2+} redox interface, this invention directly modulates the deposition thermodynamics. This results in smaller nucleation sizes, continuous nucleation behavior, and conformal MnO_2 growth across internal and external surfaces of complex 3D substrates, addressing the fundamental issue of non-uniform deposition.

2. Ultrahigh Mass Loading with Retained Scaffold Porosity.

Previous deposition methods achieved a maximum MnO_2 volumetric mass loadings of maximum 455 mg cm^{-3}, often compromising porosity in the process. Our interface design enables ultra-high MnO_2 mass loading up to 1607 mg cm^{-3} while maintaining a thin, dense, and conformal coating with thickness as low as 3.5 μm. This approach preserves much of the porosity of the 3D scaffold, representing a major

breakthrough in enabling practical thick-electrode fabrication.

3. Record-Setting Volumetric Performance for Energy Storage Devices.

Devices fabricated using our interface-engineered electrodes deliver exceptional volumetric capacitance (106 F cm^{-3} for pseudo-capacitors, 140 mAh cm^{-3} for Zn//MnO_2 pouch cells), energy density (14.7 Wh L^{-1} for pseudo-capacitors, 189.7 Wh L^{-1} for Zn//MnO_2 pouch cells), and power density (97 W L^{-1} for pseudo-capacitors, 414.5 W L^{-1} for Zn//MnO_2 pouch cells). These metrics surpass existing state-of-the-art thick electrode systems by 1 ~ 2 orders of magnitude.

4. Simultaneous Enhancement of Charge and Ion Transfer Kinetics.

By producing thinner, denser, and highly uniform MnO_2 films, our invention reduces both charge transfer resistance (both MnO_2/3DGA interface resistance Rct1 from 5.26 to 2.71 Ohm and MnO_2/electrolyte interface resistance Rct2 from 10.85 to 8.18 Ohm) and voltage hysteresis (116 mV decrease), while maintaining high gravimetric capacity at various mass loadings from 40 to 241 mg cm^{-2}. In contrast, existing approaches often suffer from trade-offs between conductivity, film thickness, ion diffusion, and mass loading.

5. Excellent Scalability and Electrochemical Stability.

Our electrodes exhibit outstanding cycle stability: over 12,000 cycles in pseudo-capacitor configurations and more than 200 cycles in Zn//MnO2 batteries at ultrahigh mass loading of 241 mg cm^{-2}.

6. Mechanistic Insights Enabled by Advanced In-Situ Characterization

For the first time, we capture and quantify the nucleation mechanism using in-situ AFM and Avrami analysis. This analysis reveals a transition from diffusion-controlled instantaneous nucleation to interface-controlled continuous nucleation, a phenomenon enabled by the VO_2^{+}/VO^{2+} manipulated interface. Such mechanistic clarity has not been demonstrated in previous work.

RELATED MATERIALS

ADDITIONAL TECHNOLOGIES BY THESE INVENTORS

- Carbon-Doped NiO Catalyst For Hydrogen Evolution Reaction
- Zinc-Iodine Battery with improved Coulombic efficiency
- Z-Scheme Microbial Photoelectrochemical System (Mps) For Wastewater-To-Chemical Fuel Conversion
- Hydrogen-Treated Semiconductor Metal Oxides For Photoelectrochemical (PEC) Water Splitting
- Self-Biased and Sustainable Microbial Electrohydrogenesis Device
- Three-Dimensional Hierarchical Porous Carbon Foams For Supercapcitors

University of California, Santa Cruz
Industry Alliances & Technology Commercialization
Kerr 413 / IATC,
Santa Cruz,CA 95064

Tel: 831.459.5415
innovation@ucsc.edu
https://officeofresearch.ucsc.edu/
Fax: 831.459.1658

© 2026, The Regents of the University of California
Terms of use
Privacy Notice