

A binder-free porous medium of interwoven CuO microstructures for energy storage

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Storage is a big challenge facing the energy sector¹. Li-ion batteries are utilized for their high energy density, low weight, and rechargeability². Anode materials are a fundamental component of Li-ion performance, impacting the overall capacity, rate capability, and device durability. While graphite is the most widely used anode material, there is a vast body of literature on new methods and materials to improve upon the above-mentioned factors³. CuO and Si are some alternatives with an increased deliverable capacity of over 2x and 10x, respectively, when compared to graphite.³ This initial capacity improvement is hindered by capacity fade after extreme volume expansion and resultant mechanical breakdown over a few cycles⁴. Numerous studies have focused on addressing this issue by forming nanostructured surfaces to allow room for expansion or incorporating binders to connect micro and nano scale particles of Si or CuO, either together or to a passive matrix of materials⁵. The former includes complex fabrication techniques⁵, while the latter approach inherently risks delamination and significant performance degradation over time. Additionally, the binder material is an extra inactive weight, reducing the specific capacity per total mass of the anode. These methods are therefore costly and slow, and unable to address the ever-growing demand for efficient and high-capacity storage.

Herein we present a simple and scalable top-down fabrication method for a binder-free porous interwoven and continuous CuO microstructure medium that is formed from an underlying Cu substrate for use as anodes in Li-ion batteries. These porous structures can be covered by a secondary layer of active material, such as Si or Ge to enhance areal capacity, without jeopardizing the porosity. A Cu substrate is used to allow for a simpler fabrication method and porosity control, a passive, room temperature etch process, employing a porous Si etch mask formed by an initial coating of an Si:Al alloy film. This etch mask is necessary to achieve high and optimal porosity with typical depth of the porous medium of $\sim 1 \mu\text{m}$. Since these structures are formed directly out of Cu substrates, they do not face delamination as they are inherently connected to the Cu current collector. We successfully demonstrate that the structured medium can be made from a deposited Cu film independent of substrate material.

¹ C. Xu, et al; "Future material demand for automotive lithium-based batteries" Communications Materials. (2020)

² M. Li, et al; "30 years of Lithium-ion batteries" Advanced Materials. (2018)

³ H. Cheng, et al; "Recent progress of advanced anode materials of lithium-ion batteries" Journal of Energy Chemistry. (2021)

⁴ M. Ko, et al.; "Challenges in accommodating volume change of Si anodes for Li-ion batteries" ChemElectroChem. (2015)

⁵ B. Kim, et al.; "Dispersion homogeneity of silicon anode slurries with various binders for Li-ion battery anode coating" Polymers (2023)

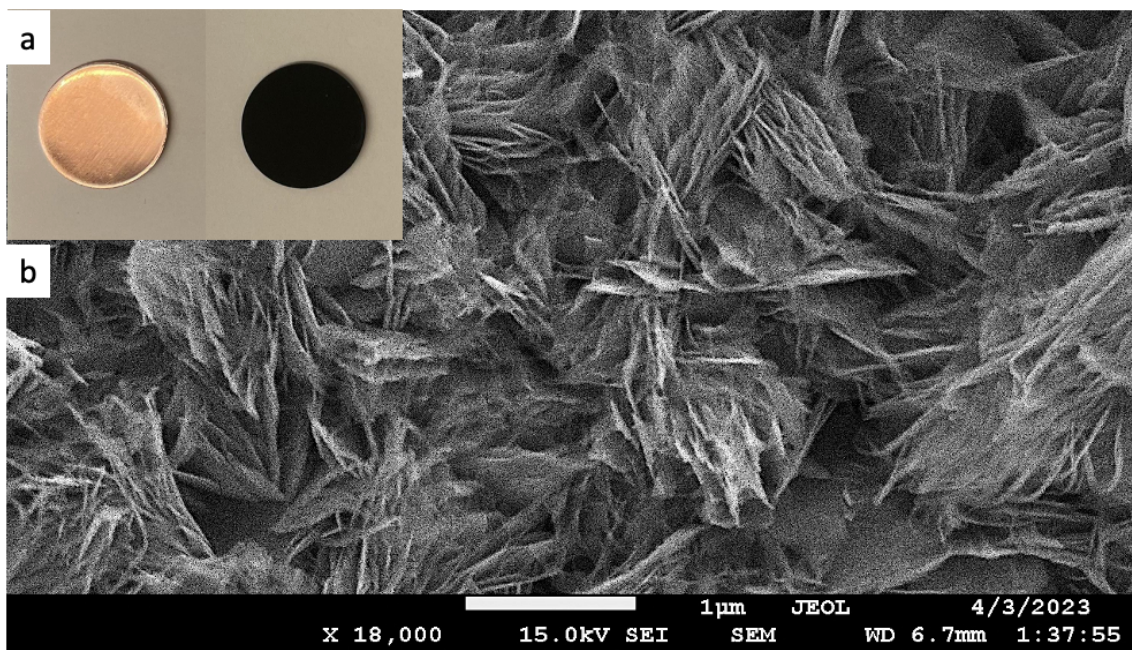


Figure 1. a) Cu disk with 15 mm diameter before and after fabrication. b) SEM of the porous CuO medium.

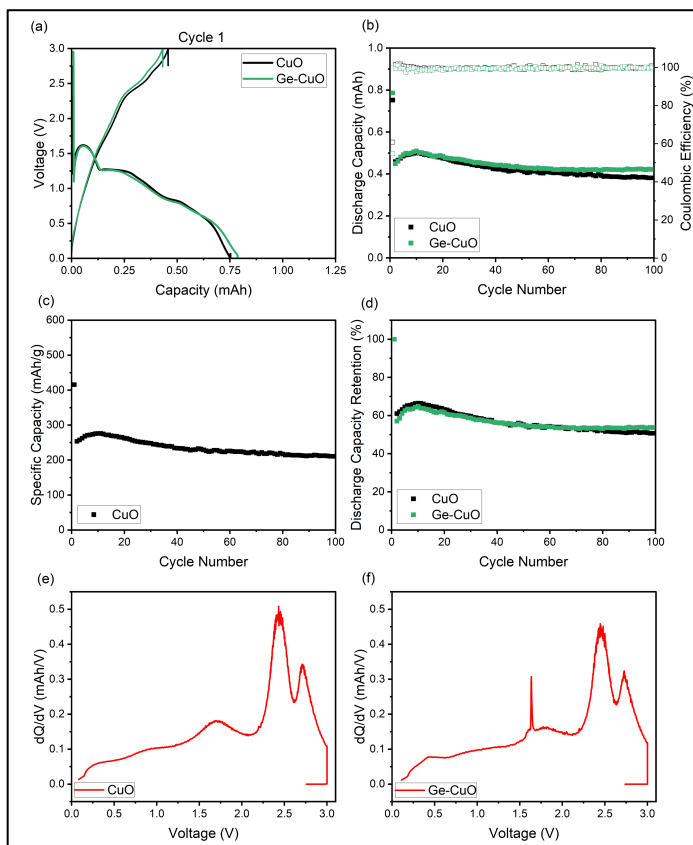


Figure 2. Galvanostatic electrochemical testing results of CuO (black) and Ge-CuO (green) cells tested at 300uA for 100 cycles between 0.005-3V. Voltage profiles for cycle one (a) and extended cycling test results with coulombic efficiency (b). Specific capacity of CuO cell (c) and capacity retention (d). dQ/dV plots on charge of cycle one for CuO (e) and Ge-CuO (f).