

Title: Investigating mass transfer relationships in stereolithography 3D printed electrodes for redox flow batteries

Authors: Maxime van der Heijden, Marit Kroese, Zandrie Borneman, and Antoni Forner-Cuenca

Redox flow batteries are a promising option for large-scale energy storage, but their stringent cost requirements hinder widespread deployment. One option to increase cost competitiveness is by improving the power density of the electrochemical cell by enhancing the performance of the porous electrode microstructure, which determines the available surface area for electrochemical reactions, electrolyte transport, and fluid pressure drop [1]. Conventional porous electrodes are fibrous mats assembled in coherent structures repurposed from fuel cell gas diffusion electrodes [2]. And, while functional, these materials have not been tailored to sustain the requirements of liquid-phase electrochemistry. Hence, new manufacturing techniques need to be developed affording a higher control over the electrode microstructure and resulting properties. Additive manufacturing, or 3D printing, is an emerging approach to manufacture controlled and deterministic architectures, enabling the tuning of electrochemical performance and hydraulic resistance [3].

In this study, we manufacture model grid structures using stereolithography 3D printing followed by carbonization (**Figure 1a**) and explore their application in redox flow batteries. We employ microscopy, tomography, spectroscopy, fluid dynamics, and electrochemical diagnostics to investigate the impact of the electrode structure on the fluid and mass transport of ordered lattice structures in non-aqueous redox flow cells. We investigate the influence of the flow field, printing orientation, and pillar geometry on mass transport (**Figure 1b**). We elucidate correlations between the electrode structure and performance metrics including pressure drop, surface area, and mass transfer correlations. We find that the printing orientation influences the electrode performance through a change in electrode morphology caused by surface roughness and resin spreading, impacting the shrinking direction after carbonization, internal surface area, and therefore the charge transfer, mass transfer, and hydraulic resistances. Moreover, mass transfer rates within the electrode are enhanced by using an interdigitated flow field or by altering the pillar shape to a helical or triangular design, which could improve mixing. Compared to commercial carbon-fiber electrodes, the pressure drop is significantly reduced (**Figure 1c**) because of the larger pore sizes ($\sim 500\ \mu\text{m}$ for the 3D printed electrode vs. $2\text{-}100\ \mu\text{m}$ for the Freudenberg H23 paper electrode and $2\text{-}300\ \mu\text{m}$ for the ELAT Cloth electrode). Whereas the commercial electrodes feature a superior internal surface area, their area-normalized mass transfer coefficients are lower compared to the printed electrodes (**Figure 1d**). Going forward, the use of additive manufacturing enabling finer features combined with carbonization at elevated temperatures can be utilized to manufacture multiscale electrodes concurrently providing excellent electrochemical performance and low hydraulic resistance. Combining additive manufacturing with emerging computational topology optimization approaches could enable the bottom-up design of advanced electrode materials for electrochemical devices [4].

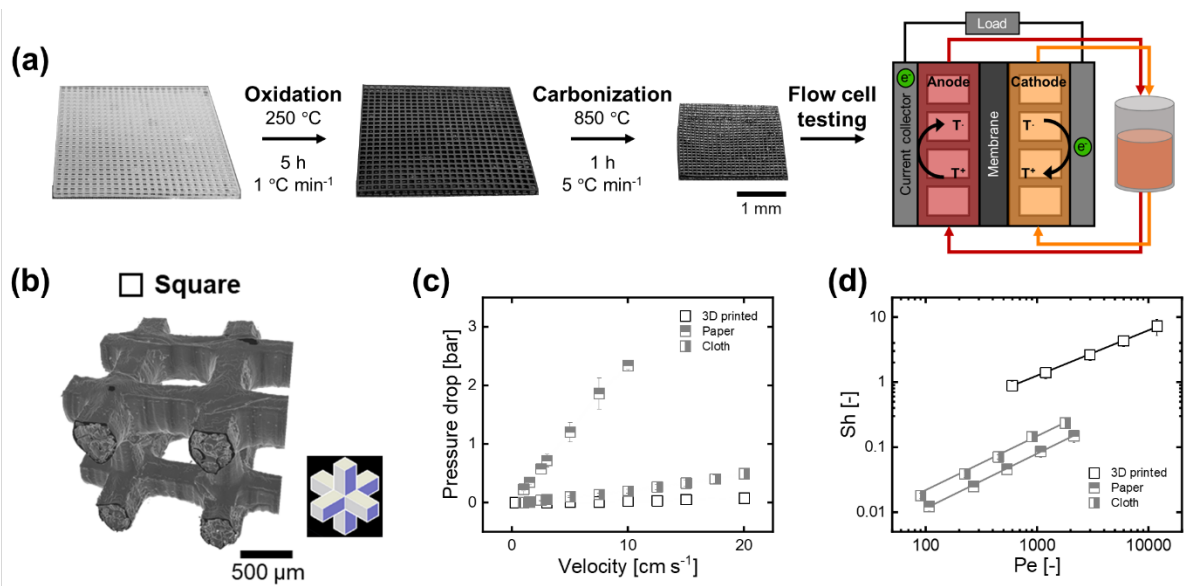


Figure 1: (a) Representation of the process workflow to obtain a conductive electrode from a nonconductive 3D print to be tested in a flow cell. (b) Subsection of the tomographic image of the 3D print after carbonization. (c) The pressure drop over a range of velocities for the 3D printed electrode and two commercial electrodes (Freudenberg H23 and ELAT Cloth). (d) The mass transfer for different superficial velocities represented by the Sherwood over the Peclet number plotted on a double-log scale for the 3D printed electrode and the two commercial electrodes.

- [1] M. van der Heijden, A. Forner-Cuenca, *Encyclopedia of Energy Storage*, 480-499 (2022)
- [2] A. Forner-Cuenca *et al.*, *J. Electrochem. Soc.*, **166**, 10, A2230-A2241 (2019)
- [3] V.A. Beck *et al.*, *Proc. Natl. Acad. Sci.*, **118**, 32, 1-10 (2021)
- [4] R. van Gorp & M. van der Heijden *et al.*, *Chem. Eng. J.*, 139947 (2022)