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Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Electrochemical Evaluation of Pyrolyzed High Aspect Ratio 3D Electrodes for Biofuel Cell Applications

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Introduction

• One way to increase the performance of a biofuel cell is to maximize the surface area of the anode and cathode. An interdigitated set-up allows a serial configuration of alternating anode and cathode and, additionally, could result in faster electron transfer due to the close proximity of the two half cells. Therefore a further optimization of the power and energy output is expected.

• Carbon 3D electrodes can be fabricated using a carbon MEMS technique in a very simple high yield process [1]. Carbonizable polymers are widely available and are typically much less expensive than metals used in thin film metal electrode fabrication. Additionally, carbon has a wider electrochemical potential window than gold and platinum [2], which is useful in e.g. biosensor applications.

Aim

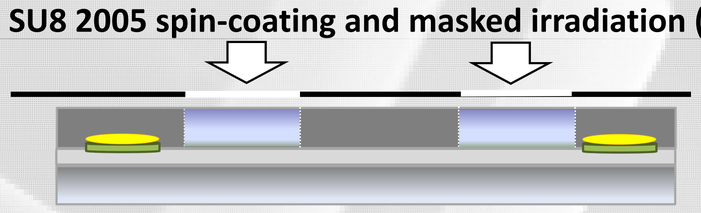
• In this work, we compare the electrochemical performance of planar interdigitated electrodes (2D IDEs) and the same IDE configuration with high aspect ratio carbon pillars (3D IDEs), using cyclic voltammetry and electrochemical impedance spectroscopy.

Fabrication of pyrolysed 3Dcarbon electrodes

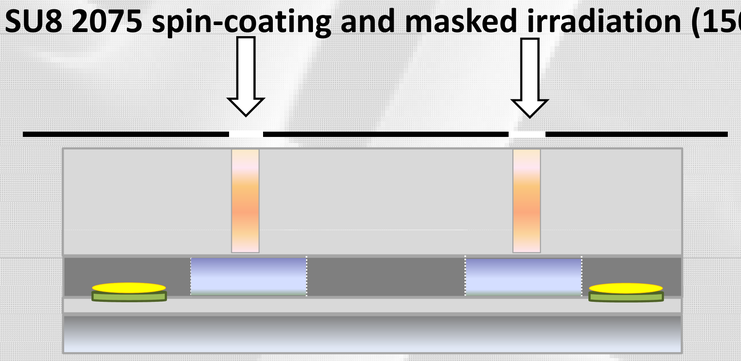
Both 2D and 3D IDEs were obtained by pyrolysis of lithographically defined negative photoresist SU-8. A two-step photolithography process was used to pattern the high aspect ratio pillars on the IDEs, resulting in a diameter of 1.4 µm and aspect ratio ~8.

(1) Cr/Au alignment marks

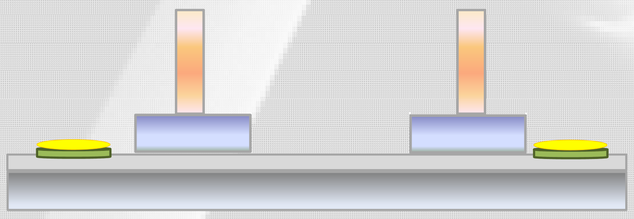
(2) 2D layer: SU8 2005 spin-coating and masked irradiation (140 mJ/cm²)



(3) 3D layer: SU8 2075 spin-coating and masked irradiation (150 mJ/cm²)



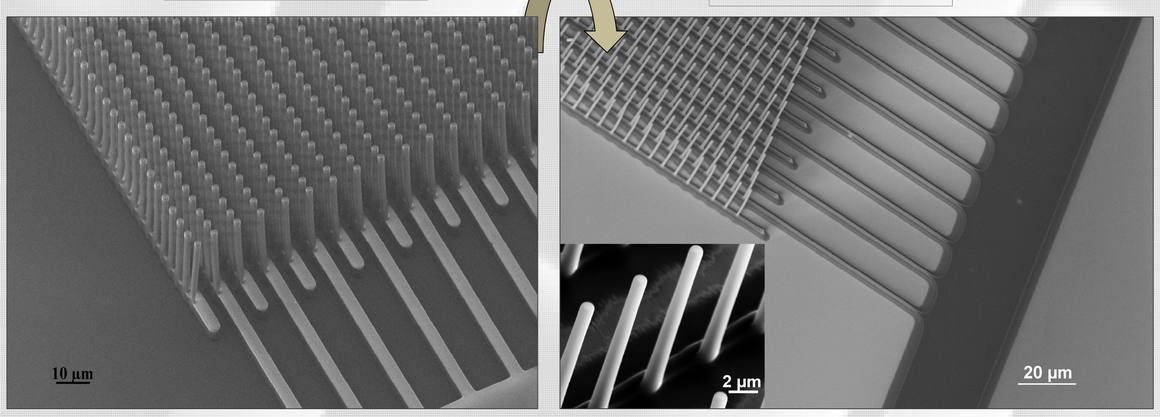
(4) Development & critical point drying



(5) Pyrolysis at 900° C in N_2 atmosphere

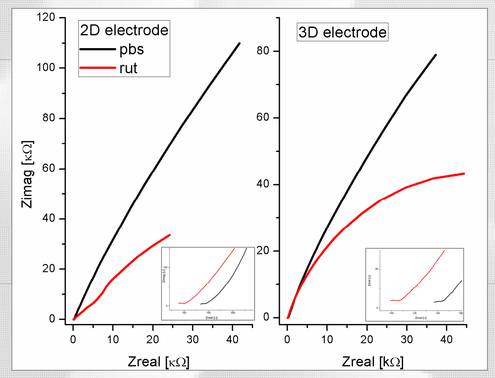
BEFORE PYROLYSIS

AFTER PYROLYSIS

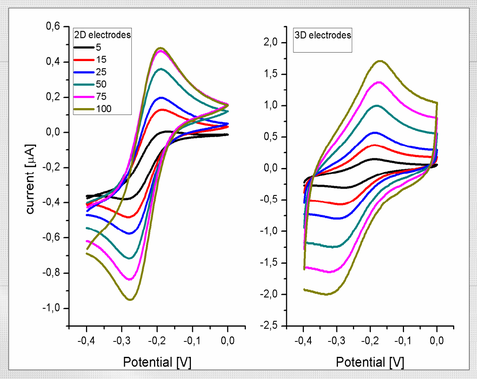


SEM images of interconnected 3D pillars on interdigitated structures before (left) and after pyrolysis (right).

Electrochemical characterization



Nyquist plots for 2D and 3D carbon electrodes in 1mM ruthenium (II/III) hexaammine (RUT) and PBS pH7. Inset: zoom-in of the impedance spectra for IDE.



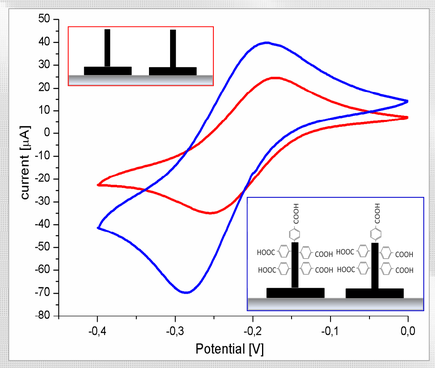
CVs of 1 mM ruthenium (II/III) hexamine chloride in PBS (pH 7) at different scan rates on 2D and 3D carbon electrodes (potentials vs. Ag/AgCl reference electrode).

• Interestingly, the semi-circle in the Nyquist plots seems to depend on the bulk properties of pyrolysed carbon, not on the solution composition, suggesting an intrinsic electroactive behaviour of the material.

• The electrodes showed resistance increase due the thin and long leads of the electrode design.

3D electrode wetting: Diazonium salt modification

3D high aspect ratio pillars have intrinsically hydrophobic properties due to their geometry. Furthermore, the surface chemistry of pyrolysed carbon contributes to the hydrophobicity of the 3D electrodes. In order to increase the wetting, the carbon surface was electrochemically modified with carboxylic groups by diazonium salt chemistry. The carboxylic acid modification of the pillars resulted in 60% increase in the peak current indicating that the wetting of the pillars was successful.



CVs of 5 mM dopamine in PBS (pH7) on pyrolysed carbon pillars: carboxylic acid-modified (blue) and bare (red) (potentials vs. Ag/AgCl RE and sweep rate: 50 mV/s).

Conclusions

• The resistivity issue related to the patterned 2D structures is being studied further.

• The wetting of the 3D electrodes can be increased by carboxylic acid modification of the carbon surface.

• This high aspect ratio carbon MEMS electrode will be excellent for biofuel cells applications and for electrochemical biosensing.

References

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[2] R. L. McCreery, in A. Bard Ed., Electroanalytical Chemistry, Vol. 7, Marcel Dekker, NY, 1991.