

Flexible And Turnable Biomimetic Pyruvate Dehydrogenase Complex (PDC) Supercapacitors

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ABSTRACT

Flexible supercapacitors are challenged by low energy density and short discharge time. We report a new type of biomimetic pyruvate dehydrogenase complex (BIMPDC) supercapacitors having the self-assembling membrane (SAM) offered a magnitude higher power, energy, and current density compared with reported flexible supercapacitors, that are based on nanobiomimetic reversible membrane potential (RPM) membrane and an asymmetric engineering design with features of flexibility and tenability under the conditions of electrolyte-free and without a metal catalyst. Two models are used for assembling the supercapacitors: Model 1 has a Au/flat “ATP Lid” bridge Membrane Electrode Assembling (MEA) and an Au/vertical “ATP Lid” nanostructure; and Model 2 has a Au/flat “Electric-Dam” MEA and an AU/nanopore “Electric-Well” nanostructure MEA. The results shown both models are turntable horizontally with three different angles from 45⁰, 90⁰ to 180⁰. They are switchable in connection from both ends having the RPM characteristics. The current density reaches 1.25 A/cm², power density is 77.4 kW/kg, and the energy density is 13.1 kwhr/kg for the bridged structured supercapacitor 1 with the specific capacitance (C_s) 54,112 F/g.

Keywords: Nanobiomimetic supercapacitor; Flexible and turntable MEA; Reversible membrane potential; Biomimetic Pyruvate dehydrogenase Complex (BIMPDC); Bridge/breathing core membrane; Asymmetric engineering design.

INTRODUCTION

Supercapacitors have two categories by energy storage mechanism: electrochemical double-layer capacitors (DLCs) and redox supercapacitors [1-3]. An approach to overcome the low Gravimetric Energy Density (GED) of the DLS supercapacitor is to use an asymmetric design: 1. the positive electrode has a low degree of polarization, and 2. the negative electrode has a high degree of polarizability in an attempt to enlarge the window of the difference of the potential change during charge and discharge [3]. After E. Chen's group developed an electrolyte-free and oxygen-independent

battery/fuel cell device [4-6], the GED and the power density performances were superior. Furthermore, Chen's group recently developed an electron-Relay prototype supercapacitor that mimics *Electrophorus Electricus*'s Reversible Membrane Potential (RPM) for multiple-organ discharge by using Nano-Biomimetic Membrane Electrode Assembling (ERNBMEA) and an asymmetric membrane design with features free from ion channeling effect and a negligible double layer potential effect was demonstrated [7-8]. The power and energy density for a single 0.2 cm³ cell are several magnitudes higher than the EE's single electrolyte of 0.03 W/kg and 0.03Whr/kg. The capacitance of the 0.2 cm³ biomimetic EE increased linearly from 0.25 to 13,240 μF/cm² over 0.015 to 1000 Hz range. At 120 Hz, the high storage capacitance is 5,140 μF/cm² that is an order of magnitude higher over the reported double-layer capacitor [8]. In consideration of the market demands for flexible supercapacitors, our focuses are to search for the special materials and prototype designs used for developing new types of supercapacitors with high power, energy and current density, yet have high flexibility.

Flexible supercapacitors are challenged by low energy density and short discharge time; hence supercapacitors usually can not be used alone for power automobiles. They have to be combined with batteries together to power automobiles. Excellent review literature in supercapacitors emphasized the needs for new materials and new device designs were published [9-11]. Therefore, again, our eyes are turned to nature and learn its secret in produce energy. Pyruvate Dehydrogenase Complex (PDC) exists mainly in mitochondrial cells in the brain and kidney and reproductive organs, and PDC is the key mitochondrial metabolic enzymes and it is responsible for the production of cellular energy in the form of ATP. Three-dimensional structure analysis of PDC revealed its highly symmetric structure exists with a hollow truncated cube with an edge of 125Å, forming the core of the multienzyme complex [12]. Crystal structures of PDC revealed the hydrophobic interactions occur mainly in the lipoyl binding pocket in PDK3. These structural components formed a deep cylindrical pocket with hydrophobic residues. There is a dynamic equilibrium between completely disordered vertical ATP lid and a relatively ordered flat ATP lid for the purpose of easily

release ADP and for trap ADP [13]. Z. H. Zhou's paper also revealed the flexible bridge exists within the truncated E2 core [14]. The goal of this research is to develop a nanostructure flexible biomimetic "ATP Lid" of PDC supercapacitor with an engineering asymmetric design for an attempting to enhance an order of magnitude performance in power, energy and current density compared with conventional approaches.

EXPERIMENTAL

Fabrication of the Nanostructured Biomimetic PDC Conformational "ATP Lid" Self-Assembling Membranes (SAM)

The nanostructured biomimetic PDC SAM with the vertical bridged conformational "ATP Lid" was freshly prepared. Polyethylene glycol diglycidyl ether (PEG), triacetyl- β -cyclodextrin (T-CD), poly(4-vinylpyridine) (PVP) were purchased from Sigma. PVP was purified before use. The mono imidazol derivative dimethyl β -cyclodextrin (mM- β -DMCD) was generally synthesized according to the published procedures [15]. The appropriate amount of solutions of individual polymer and reagents were prepared [16]. The mixture solution was made up by mM- β -DMCD, T-CD, PEG and PVP. The gold electrode (50 nm) was coated on a polymer substrate, and the above mentioned mixture solutions was injected onto the surface of the gold electrode. The MEA was incubated for 48 hrs at 35°C [16].

The nanostructured biomimetic PDC SAM with the flat bridged conformational "ATP Lid" was freshly prepared by adding appropriate amount of *o*-nitrophenyl acetate (*o*-NPA) into the above described mixture solution for the vertical bridged PDC SAM. All other procedures were followed as cited in literature 16.

Characterization of the Membrane

The morphology of the AU/SAM was characterized using a Atomic Force Microscope (AFM) (model Multimode 8 ScanAsyst, Bruker, PA). Data Collected in PeakForce Tapping Mode. Probes used were ScanAsyst-air probes (Bruker, PA). The silicon tips on silicon nitride cantilevers have 2-5 nm radius. The nominal spring constant 0.4N/m was used. Figure 1 illustrates the 3D vertical conformational PDC bridge structure with "breathing nanopore" of the AFM images of the Biomimetic "ATP Lid". Figure 2 illustrates the 3D flat conformational PDC bridge structure with "breathing nanopore" of the AFM images of the Biomimetic "ATP Lid"

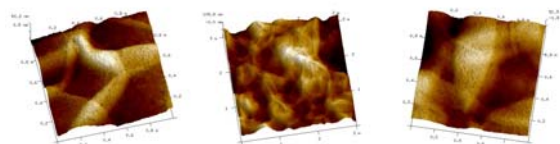


Fig 1. 3D vertical conformational PDC bridge structure of the AFM images of the Biomimetic "ATP Lid".

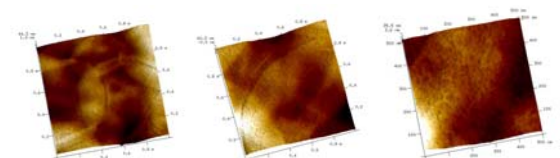


Fig 2. 3D horizontal conformational PDC bridge structure of the AFM images of the Biomimetic "ATP Lid".

Asymmetric Design of the Supercapacitor

An asymmetric design for the Biomimetic PDC "ATP Lid" vertical and flat bridge as model 1 shown in Figure 3. One electrode with AU/vertical "ATP Lid" bridge having nanopore for a "breathing" MEA, and the other MEA was with a flat "ATP Lid" bridge with a "breathing pore". An insulator was placed between the two MEAs and absorbed with 1M methanol under electrolyte-free condition. The current collectors were attached at the each end. This design was used for model 1.

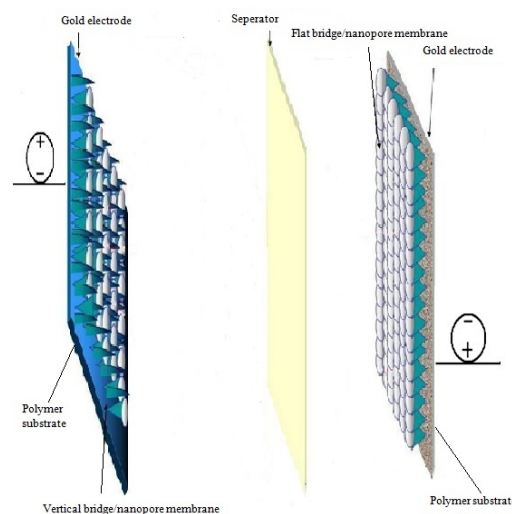


Fig 3. Illustrates the asymmetric design of the flexible supercapacitor. The vertical "ATP Lid" bridge/nanopore membrane self-assembling on the gold electrode (Left), and the flat "ATP Lid" bridge membrane with nanopore of "breathing" on gold electrode (Right).

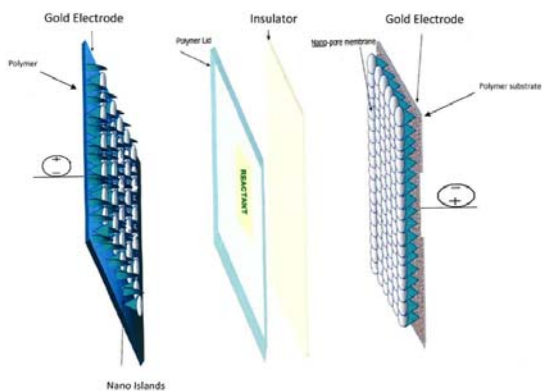


Fig 4. Illustrates the asymmetric design of the flexible supercapacitor. The “Electric-Dam” MEA (Left) and “Electric-Well” MEA on the right is shown.

Model 2 design was carried out as shown in Fig 4. It is an asymmetric design with a nano islands structure with a lid of “Electric-Dam” [7-8] and separated by an insulator as same as model 1, and another MEA is a nanopore only as “Electric-Well” configuration [17].

RESULTS AND DISCUSSIONS

Fast RPM Charge/Discharge Rate

Figure 5 illustrates the fast discharge and charge profiles for model 1 (Left) with features of RPM, and model 2 is shown (Right) with RPM characteristics at ± 1 mA.

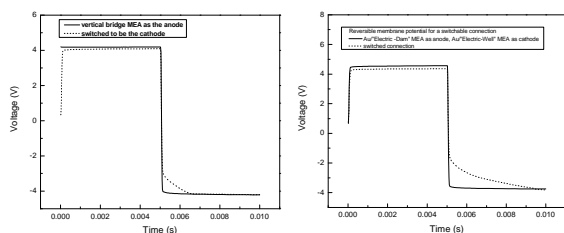


Figure 5 illustrates the fast discharge and charge profiles from a single 0.04 cm^2 prototype device for model 1 (Left) with features of RPM, and model 2 is shown (Right) with RPM characteristics at ± 1 mA.

Tunable and Flexible

Supercapacitors are turnable increased flexibility as show in Figure 6, left is for model 1 and right is for model 2. The turn ability will enhance the portability.

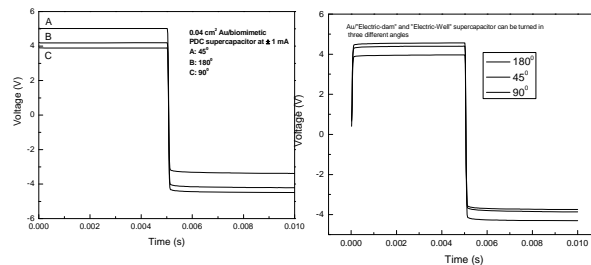


Fig 6 illustrates the turn ability and flexibility. The current collectors connected with two MEAs turned in different angles of 45, 90 and 180° horizontally with model 1 in (L) and model 2 in (R).

High Power and Energy Density

The two models of supercapacitors had a DC current -50 mA discharge for 12 hrs in a 0.04 cm^2 device with a current density of 1.25 A/cm^2 . Power density is 77.4 kW/kg using the equation of $p = V^2/4RM$; Energy density is 13.1 kWhr/kg using the equation of $E = I \times \text{hr} \times V/m$, m is the device weight in kg, V is the normal discharge voltage and I is current in A for model 1. Model 2 results are similar with slightly less than model 1. Both models have improved the supercapacitor performance compared with our former reported non flexible supercapacitors [7-8].

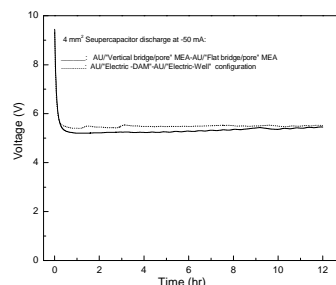


Fig 6 Illustrates the discharge profiles for model 1 (solid line) and model 2 (dotted line).

High Capacitance

The charge/discharge profiles from the two models supercapacitor are shown in Figure 7 at $\pm 1 \text{ mA}$ over the band width from 0.015 Hz to 1000 Hz using the Double Step chronopotentiometry (DSCPO) method. Figure 7 illustrates the plots of capacitance vs. frequency with Model 1 (L) and Model 2 (R). Over the $0.015 - 1000 \text{ Hz}$ band width, bridge structured supercapacitor’s capacitance is $308 \mu\text{F/cm}^2$ at 20 Hz ; The specific capacitance (C_s) for the bridge structured supercapacitor is $54,112 \text{ F/g}$, that was calculated according to equations used in literature [18], which is two orders of magnitudes

higher than the reported performance [10]. Both model supercapacitors have good performance as shown in Figure 8 (Left, Model 1) and Model 2 on the right.

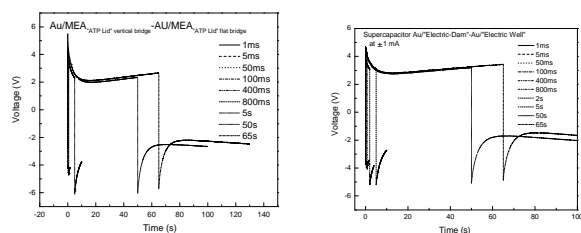


Figure 7. Illustrates the supercapacitor charge/discharge profiles over the band width from 0.015 Hz to 1000 Hz at 9 increment levels (Model 1, L; Model 2, R).

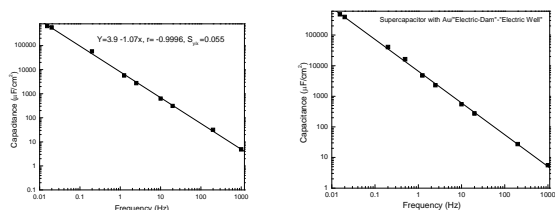


Figure 8. Plot of the capacitance versus frequency (Hz) of the supercapacitor (model 1, L) and model 2 (R), assuming a series RC circuit model.

Energy Contour Map

Energy density dependency on nominal discharge voltage and special capacity of the supercapacitors were plotted according to the results obtained in Fig 6. Fig 9 on the left shown the model 1 has the high energy density positively correlated with a full range of voltage and with higher capacity is revealed. The plot for model 2 shows high energy density correlated with high capacity at low discharge voltage. The comparison has shown the advantage of the “ATP Lid” structure model 1 over model 2.

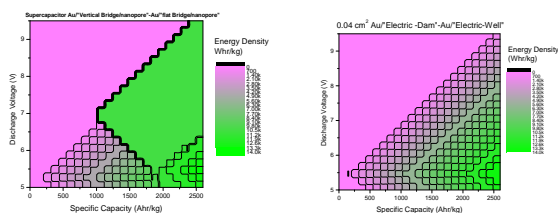


Fig 9 illustrates the multiple variable contour map for the energy density dependency with Model 1 on the left and model 2 on the right at -50 mA 12 hrs discharge.

CONCLUSIONS

The flexible biomimetic PDC approach and asymmetric design providing high power, energy and current density and a magnitudes higher capacitance may further pave the road for product development.

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