

Asymmetric RuO₂/Pt Cells as Hybrid Micro-Capacitor/Fuel-Cell Systems

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Hydrous ruthenium oxide (RuO_xH_y or RuO₂•xH₂O) exhibits high specific capacitance and is an excellent charge-storage medium for ultracapacitors.¹ The material can be difficult to implement in practical electrodes, because it is prone to self-discharge and potential recovery, particularly in aqueous solutions. Self-discharge is the loss of potential by a charged electrode, and potential recovery is the increase in potential of a discharged electrode. We have studied the pervasive self-discharge and potential-recovery mechanisms, and now attribute them respectively to the oxidation of hydrogen and reduction of oxygen molecules that are present in dilute concentrations in the electrolyte.

Although the self-discharge and potential recovery of charged symmetric electrochemical capacitors cause a decrease in the cell voltage to zero over time, the mechanisms can be used constructively to generate micropower from asymmetric cells. Specifically, we use hydrous RuO₂ as a positive electrode (cathode) and Pt as a negative electrode (anode) to make a cell that produces micropower from scavenged oxygen and hydrogen. The amount of power produced is higher than what is expected from solely atmospheric H₂ (nominally 5 ppm), suggesting that additional fuel is created by the thermal and/or photodecomposition of water.

Single cells have open circuit voltages on the order of 0.3 V in 0.1 M H₂SO₄ from the difference in the potentials of the hydrous RuO₂ and Pt electrodes (approximately 1.0 and 0.7 V vs RHE, respectively). Because the hydrous RuO₂ stores charge, the cells can either be discharged rapidly at staged intervals (from 1 to 300 min) or they can be constantly drained in fuel cell mode at low levels of current. Cells can be assembled in series or in parallel to increase the cell voltage or current.

Figure 1 shows the discharge of a four cells in parallel with a positive electrode of hydrous RuO₂ on tantalum and a negative electrode of Pt in 0.1 M H₂SO₄. The cells are discharged every 5 min at 50 μA from 0.3 to 0.1 V in 100 ms to yield 10 μW bursts of power (total surface area of the positive electrodes is 0.96 cm² for a normalized power of 10 μW/cm²). Figure 1a shows the behavior of the cycles to 240 min (the cell was cycled to 480 min with no decrease in performance), and Fig 1b shows a magnified view of a single discharge-recharge cycle. The system recharges to the original cell voltage during a 5 min rest period due to the electrocatalytic conversion of scavenged hydrogen and oxygen, and the charge is stored in or on the surface of the electrodes.

The behavior of the cells in seawater and tap water is impressive. We have recently shown that four cells in parallel can be discharged at 500 μA from 0.24 to 0.09 V in 360 ms every 5 min to yield 75 μW or 50 μW/cm². These data give us confidence that the electrodes would be useful in “real world” applications and not restricted to use in laboratory-grade solutions.

Lastly, we are striving to take advantage of the enhanced diffusion offered by microelectrodes. This

concept is being evaluated with arrays of 20-μm-wide interdigitated electrodes of hydrous RuO₂ and Pt.

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References

1. J.P. Zheng, P.J. Cygan, and T.R. Jow, *J. Electrochem. Soc.*, **142**, 2699 (1995).
2. T. Liu, W. G. Pell, and B. E. Conway, *Electrochim. Acta*, **42**, 3541 (1997).

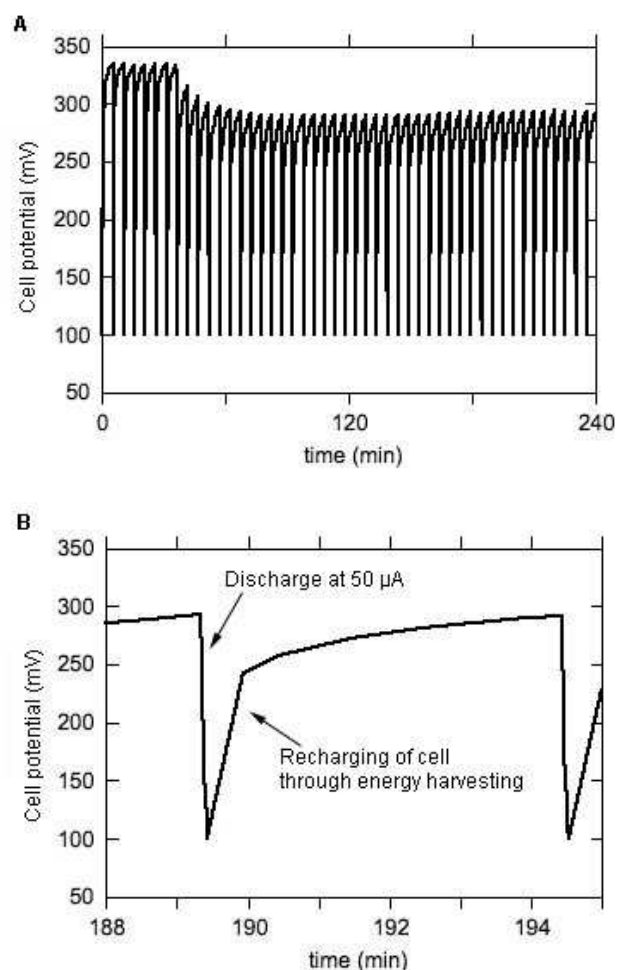


Figure 1. Discharge of an electrochemical cell with hydrous RuO₂/Pt electrodes every 5 min for 240 min at 50 μA in 0.1 M H₂SO₄; (b) expanded view of a selected cycle showing the discharge of the cell and then the spontaneous recharging process that occurs under no load due to the oxidation and reduction of scavenged H₂ and O₂ at the negative and positive electrodes, respectively.