

Semiconductors as selective electrodes for Bio-photovoltaic cells.

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The bio-photovoltaic (Bio-PV) cell proposed by Takshi et al. [1] and illustrated in Figure 1, incorporates solar energy harvesting and storage in a single electrochemical device. Bacterial photosynthetic Reaction centres (RCs) capture photons, separate charges and maintain charge separation for long times (~1ms to 1s). The charges are then extracted and shuttled by mediators (m_1 and m_2) to opposite electrodes. Under open circuit conditions, energy is stored in the reduced/oxidized mediator states.

Modelling results suggest a possible efficiency of 20% with electrodes that have high redox selectivity (~5 orders of magnitude) for one mediator in solution. Selectivity has been discussed in the context of photogalvanic cells [2] but the approach presented here has not been investigated systematically.

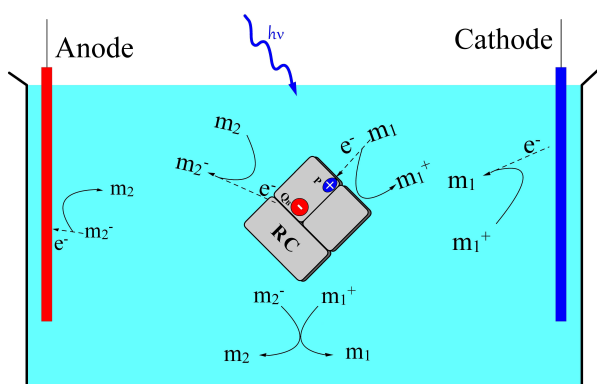


Figure 1 Bio-PV cell showing role of RC and mediators.

Semiconductors offer one avenue for obtaining selective electrodes. Semiconductor and redox couple reactions rates are governed by the overlap between energy levels in both systems. As shown in Figure 2, a redox couple with a large conduction band overlap should have higher redox reaction rates compared to one that overlaps the semiconductor bandgap.

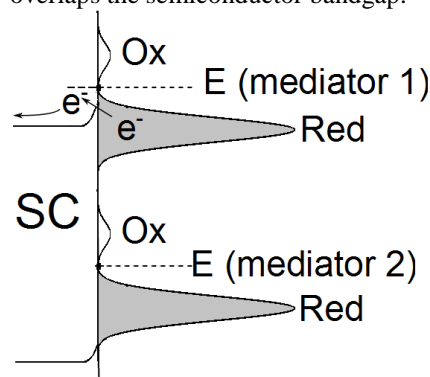


Figure 2. Semiconductor-electrolyte interface energy alignment. Larger conduction band and redox potential separation should lead to slower reaction rates.

This work reports selectivity observed using a Fluorine doped Tin oxide (F:SnO₂) electrode with Methyl Viologen (MV) compared to Ferricyanide/Ferrocyanide (Fe(CN)₆) and Ferric/Ferrous (Fe³⁺/Fe²⁺) redox couples.

Figure 3 shows cyclic voltammetry (CV) curves with F:SnO₂ and aqueous MV, Fe(CN)₆ and Fe³⁺/Fe²⁺

solutions. The relative peak magnitudes and separations show a preferential reaction between F:SnO₂ and MV.

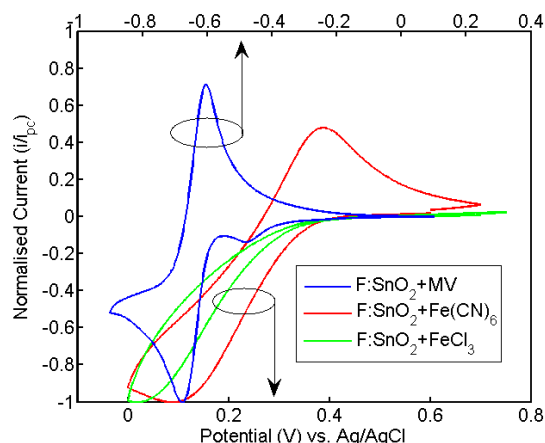


Figure 3 CV for SnO₂ and multiple mediators at a scan rate of 10 mV/s. Current axis is common and potential axes are as marked. Currents are normalised to the cathodic peak current.

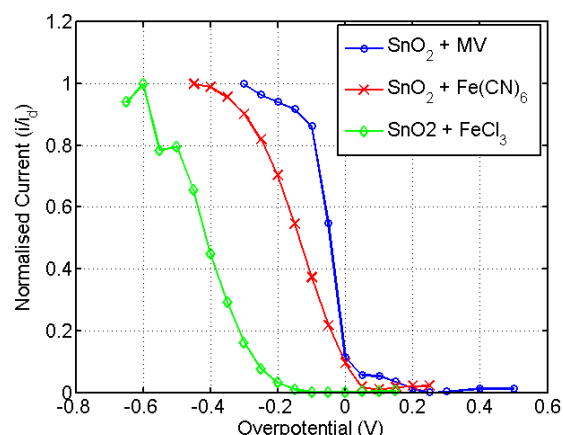


Figure 4 Sampled current Voltammetry between SnO₂ and multiple mediators. Currents are normalised to the diffusion current.

Sampled current voltammetry data is shown in Figure 4. It is seen that MV reaches the mass transport region at significantly lower overpotentials than Fe(CN)₆ and Fe³⁺/Fe²⁺. Reaction rates were estimated from these plots and are listed in Table 1.

Table 1 Rates of reaction of mediators with F:SnO₂ electrode. E_{cb} is the F:SnO₂ conduction band edge vs. the vacuum level.

Mediator	E_0 (vs Vac.) (eV)	$E_{cb} - E_0$ (eV)	k_0 (cm/s)
MV	4.1	~0	1.1×10^{-4}
Fe(CN) ₆	4.7	0.6	6.0×10^{-6}
Fe ³⁺ /Fe ²⁺	5.2	1.1	2.0×10^{-7}

Table 1 shows that the rate of reaction varies inversely with the difference between F:SnO₂ conduction band and the mediator redox potential. Approximately two to three orders of magnitude difference in the reaction rates is observed in this case. By choosing an appropriate semiconductor and redox couple, it may be possible to achieve higher selectivity towards one redox couple. Future work on p-type CuO electrodes mediators should validate this method of achieving selectivity.

References:

- [1] Takshi, A., Madden, John D.W. and Mahmoudzadeh, A., Saer, R., and Beatty, J. T., *Energies*, 2010, Vol 3, Pg 1721-1727.
- [2] W. J. Albery and M. D. Archer, *J. of The Electrochem. Soc.*, 1977, Vol 124, Pg 688-697.