Optimizing Turnover of a Metallopolyion-Coated Electrode in a Flow Cell in Microemulsions

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Electrodes with immobilized catalyst layers have been explored in our laboratory for green electrochemical synthesis using microemulsions rather than toxic organic solvents. Vitamin B12 hexacarboxylic acid [$B_{12}(COOH)_6$] attached to poly(L-lysine) [PLL] covalently bound to graphite electrode surfaces has been used for variety of organic reactions such as alkylation and dehalogenation[1]. Turnover numbers for catalytic conversion of trans-1,2-dibromocyclohexane [DBCH] to cyclohexene using film electrodes were dramatically larger than in solution phase catalysis[1] because of more efficient use of the catalyst in the immobilized form. Additional catalyst film thickness can increase catalytic efficiency provided films are not limited by charge transport and/or mass transport. Cyclic voltammetric studies of these films in SDS microemulsions showed increasing electroactive surface concentration only up to about 160 nm thick. The rotating disk voltammetry showed higher catalytic efficiency compared to cyclic voltammetry due to convective mass transport [Figure 1] indicating these films may work better under efficient mass transfer conditions[2] but optimum catalytic efficiency was found for films of about 18 nm thick. Under batch conditions, the efficiency of the catalysis was limited by mass transport of reactant.

Performance of these films for synthetic applications was evaluated for electrolysis of DBCH in a plate and frame type flow cell. The high reaction rates requiring higher mass transport to the electrode surface could be readily achieved using turbulence promoters and control of linear electrolyte velocity. Turnover numbers and current efficiency values in microemulsions obtained for electrolysis in the flow cell and in a conventional laboratory stirred batch cell indicated that multilayer films of [$B_{12}(COOH)_6$]-PLL can be efficiently used for catalyzing variety of organic reactions and work without any mass transfer limitations if employed in efficient electrolyzer [Figure 2&3]. Optimum film thickness for Batch cell was 18 nm where as Flow cell operated well even at 90nm film thickness.

References

1. Zhou, D.-L., Njue, C.K., Rusling, J.F., *J. Am. Chem. Soc.*, 121 (1999) 2909-2914.
2. Campbell, C.J., Njue, C.K., Nuthakki, B., Rusling, J.F., *Langmuir*, 17 (2001) 3447-3453.

Figure 1: Catalytic Voltammetry of PLL-B12 films in CTAB microemulsion with single catalyst layer

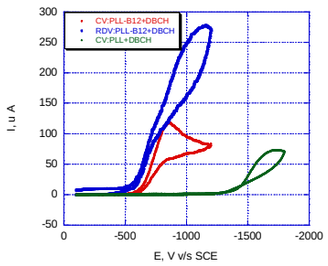

Figure 2: Constant Current Electrolysis at different catalyst concentration
Variation of Current Efficiency at different I/C for DBCH reduction in CTAB microemulsion

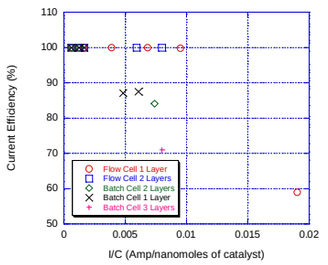

Figure 3: Current Efficiency v/s Turnover Number
DBCH reduction in CTAB microemulsion at different I/C