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TECHNICAL NOTE

Indirect high current density reductions using cathodically generated solvated electrons

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It is usually economically desirable in view of the high capital cost of plant and high interest rates, to perform electrosyntheses at high current densities. However, the rate of mass transfer often prevents the optimum value being achieved, particularly when the concentration of the substrate has to be kept low due to solubility or mechanistic reasons. Many attempts have been made to develop compact electrodes with large surface area to overcome this difficulty e.g. porous electrodes, slurry electrodes, particulate electrodes.

In situations where indirect reaction is feasible, e.g. oxidation via a higher valency state of a transition metal [1], then a high current density can be achieved by using a high concentration of the intermediate, namely, the corresponding metal ion. The limiting factor then becomes the diffusion limited rate of mass transfer of the metal ion through the boundary layer. In the case of indirect reductions using electrochemically generated solvated electrons [2] the situation is even more favourable. Owing to the very high mobility of solvated electrons which, at high concentrations, is several orders of magnitude higher than for normal species [3], very high rates of electron transfer can be achieved through the stagnant boundary layer and gentle stirring suffices to balance this rate with the subsequent homogeneous reaction.

Reductions using solvated electrons produced at very high controlled current densities in the presence of low concentrations of an organic substrate were performed in the hexamethylphosphoramide (HMPA)/lithium chloride system using the reduction of anthracene as the model reaction. The results obtained for the same system at low current densities are given elsewhere [4] together with the experimental details. For the present case, a 0·3 M solution of LiCl in HMPA was employed and the concentration of the proton donor, i.e. acetic acid, was kept at around 10 mM by adding microlitre amounts as the process progressed. A two-compartment cell was used with a vitreous carbon cathode (area = 0·08 cm^2) and a platinum foil anode. Only a moderate rate of stirring was necessary to disperse the solvated electrons, and when sufficient current had been passed to reduce all the anthracene to the hexahydro-derivative, the whole catholyte became blue. Throughout each run the product composition was monitored using VPC. The results are shown in Table 1.

These show that up to the highest current density employed, 1 A cm^{-2}, the anthracene was efficiently reduced with no significant drop in coulomb yield. As a measure of the utility of the indirect reduction, a calculated scale-up factor is included in the table for each experiment. This factor is the ratio between the actual current density employed and the maximum diffusion limited value that would be observed if anthracene could be reduced directly at the cathode in a six-electron process.

The use of this indirect reduction process at high current density raises the problem of the anodic reaction. Most organic reduction processes require the supply of one proton for each electron consumed. It would be convenient to supply these from the anodic reaction. A suitable anode for this can be made from the hydrogen/

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Table 1. The reduction of anthracene at high current densities

Anthracene conc., mM.	*Experimental current density, mA cm^{-2}*	*Calculated diffusion limited current mA cm^{-2}*	*Coulomb yield %*	*Scale-up Factor* i_{exp}/i_{diff}
2·0	125	0·72	44·5	174
1·5	625	0·54	44·0	1160
1·0	1000	0·36	43·5	2780

palladium system, which has the additional advantage of being able to sustain quite high current densities at potentials such that the organic substrate is unlikely to be oxidized, thus eliminating the need for a separator. A simple cell structure based on concentric tubes down which the electrolyte containing the substrate would be pumped is shown in Fig. 1. This arrangement allows suitable scaling of the relative areas of anode and cathode. In the structure shown, a palladium/silver membrane acts as anode for the solvated electron cell and as cathode in the outer aqueous system which is the primary source of protons. Although this cell has not yet been tested, preliminary experiments have been carried out in a simplified system comprising a single compartment cell with a vitreous carbon cathode and palladium foil anode 0·1 mm thick which had been precharged with hydrogen. The cathode current density was maintained at 1 A cm^{-2} and the reduction of anthracene was again used as a model. In these experiments detailed in Table 2, either acetic acid or sodium acetate was added as proton carrier to facilitate transport of protons from the anode to the cathodic reaction zone. It can be seen that the coulomb yields were satisfactory so long as the substrate concentration was not too low. At low substrate concentrations the lifetime of the solvated electrons was sufficiently long to enable them to be reoxidized at the anode. In these preliminary experiments, no attempt was made to minimise this effect nor to achieve optimum conditions.

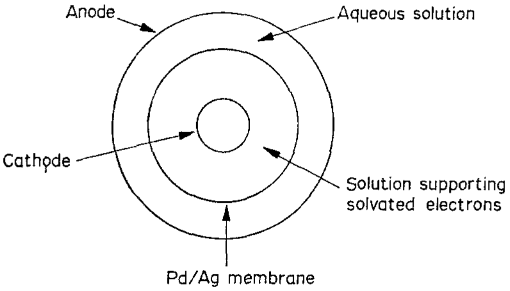

Fig. 1. Cross-sectional view of a concentric cylindrical cell for reductions at high current density using solvated electrons.

Table 2. Reduction of anthracene at 1 *A cm^{-2} using a Pd/H$_2$ anode as the proton source*

Anthracene conc., mM	*Sodium acetate conc., mM*	*Acetic acid conc., mM*	*Coulombs passed*	*Coulomb yield %*
1	10	0	10	10·0
10	10	0	90	30·5
			200	34·0
1	10	0	20	13·5
			40	11·0
10	0	10	50	45·6
			150	33·0
1	0	5	20	12·2

Solvated electrons can be readily generated in a variety of solvent systems and it might be desirable to use this indirect method of reduction in order to achieve high current densities even when direct electrode reduction is possible.

References

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