

## SOME TECHNIQUES OF PRACTICAL INTEREST IN ELECTROLYSIS

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In the preparation of inorganic and organic chemicals and in the winning of metals by electrolysis, a number of techniques have been adopted, mainly from the point of view of achieving high efficiency in the process and also with a view to scale up the process for commercial scale production. Some of the techniques are described in the literature but have not been investigated thoroughly for adopting them from a commercial point of view. During the last more than 25 years of investigation carried out, the author has been able to try out a few techniques in electrolysis which have proved to be of advantage in commercialising processes which could be implemented on a commercial scale.

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### ELECTRO-ORGANIC CHEMISTRY

#### *Electrode Rotation*

The capacity of a given electrolytic cell is directly proportional to the current. This can be increased by providing higher electrode surface area per unit volume or by increasing the range of operating current densities by overcoming the limitations posed by the external factors especially the mass transfer of the substrate. By rotating the working electrode (Udupa & Dey, 1955 & 1956), the mass transfer would be increased manifold especially in diffusion controlled reactions. By this, the operating current density could be increased without affecting the efficiency of the reactions and in some cases leading to the product selectivity. Knowing the conditions for the reactions to take place favourably, one can very easily come to the conclusion whether cathode rotation is going to be favourable or not for the reaction. One such reaction which has been studied is the reduction of salicylic acid to salicylaldehyde at an amalgamated cathode (Dey & Udupa, 1953; and Udupa & Dey, 1955). Electrolysis is carried out in Sodium sulphate solution containing boric acid at a  $pH$  of 6. The reduction of the salicylic acid is supposed to take place by a reaction with the sodium amalgam formed (Satyanarayana & Udupa, 1959) by electrolysis. This would result in an increase of the cathode film  $pH$  so that the salicylic acid molecule is not able to approach the cathode surface because of the formation of salicylate anion which is repelled at the cathode. Cathode rotation helps in maintaining the  $pH$  of the diffusion layer at the desired value and

reduction takes place with high efficiency especially at high current densities. At a stationary cathode using a stirrer only 10 per cent efficiency can be obtained whereas with cathode rotation (Udupa, 1961), 50–55 per cent current efficiency can be achieved at a current density of 12 Amp/dm<sup>2</sup>.

In the reduction of nitro-benzene to *p*-aminophenol in acid medium (Krishnamoorthy *et al.*, 1956) the reduction proceeds through the intermediary stages of nitroso benzene and phenyl hydroxylamine and the latter undergoes rearrangement in acidic medium to *p*-aminophenol. Phenyl hydroxylamine can rearrange to *p*-aminophenol if it is rapidly allowed to react with the acid. If it continues to remain in the diffusion layer, it can undergo further reduction to aniline. Cathode rotation thus favours *p*-aminophenol transformation to aniline formation (Christopher Wilson & Udupa, 1952). A number of nitro-compounds have been studied using the stationary and rotating cathodes. In all the cases, *p*-aminophenol formation as a product is enhanced by cathode rotation as seen from Table I.

TABLE I

*Reduction of aromatic nitrocompounds to corresponding aminophenols*

Catholyte	350ml 20 per cent H <sub>2</sub> SO <sub>4</sub>
Anolyte	150ml 20 per cent H <sub>2</sub> SO <sub>4</sub>
Temperature	90 °C
Current density	2.7Amp/dm <sup>2</sup>
Cathode	Amalgamated copper
Anode	Lead

Nitrocompound reduced	Motion of cathode	Percentage yields of	
		Aminophenol	Amine
Nitrobenzene	Rotation	71.7	6.6
”	Stationary	56.5	10.6
2-Nitro-6-chloro-toluene	Rotation	82.8	8.5
”	Stationary	45.6	27.2
2-Nitro-4-chloro-toluene	Rotation	81.7	4.85
”	Stationary	43.8	26.4
<i>o</i> -Nitrotoluene	Rotation	73.5	7.7
”	Stationary	55.5	10.3
<i>o</i> -Nitrochlorobenzene	Rotation	75.8	4.95
”	Stationary	50.1	17.5
2:5 dichloro-nitrobenzene	Rotation	71.9	7.2
”	Stationary	44.3	26.0

Reduction of nitro compounds (Udupa *et al.*, 1961) to hydrazo compounds in alkaline medium using a spongy lead-deposited mild steel cathode could be carried out at very high current densities even though the nitro compound is insoluble in the electrolyte and the product formed is a solid. Cathode rotation produces turbulence and the electrolyte gets saturated with the nitro compound so that the

availability of the reactant at the interface is enhanced and the removal of the solid product from the electrode surface is also favoured as seen from Table II. A number of nitro compounds like *o*-nitro anisole (Udupa *et al.*, 1962) *o*-nitro toluene, *o*-nitro chloro-benzene (Udupa *et al.*, 1961) have been studied initially on a laboratory scale and later in a scaled-up cell at 3000amp capacity (Balakrishnan *et al.*, 1969; and Udupa *et al.*, 1972) and very high yields of the corresponding hydrazo-compounds obtained, as seen from Table III.

TABLE II

*Effect of current densities on the reduction of nitrobenzene in sodium hydroxide medium*

Catholyte	:	10 per cent NaOH
Anolyte	:	30 per cent NaOH
Temperature	:	80-85 °C
Anode	:	Nickel plated m.s.
Diaphragm	:	White asbestos cage

Current density (A/dm <sup>2</sup> )	Mode of Cathode	Yield of hydrazo- benzene (%)
5	Rotation	86.5
5	Stationary	...
10	Rotation	87.1
10	Stationary	13.5
20	Rotation	88.0
20	Stationary	10.7
25	Rotation	88.5
30	Rotation	88.2

TABLE III

*Products formed during the reduction of nitrocompounds in alkaline medium*

Catholyte	:	10 per cent NaOH
Anolyte	:	30 per cent NaOH
Temperature	:	80-85 °C
Anode	:	Nickel plated m.s.
Cathode	:	Rotating lead deposited m.s.

Nitro- compound	Current density (A/dm <sup>2</sup> )	Yields of		
		Benzidines (%)	Azo compound (%)	Amines (%)
Nitrobenzene	30	80.0	7.3	6.1
<i>o</i> -Nitrochlorobenzene	25	82.2	...	9.8
<i>o</i> -Nitroanisole	30	70.2	19.7	7.8
<i>o</i> -Nitrotoluene	20	55.0	23.0	12.9

The reduction of benzoic acid to benzyl alcohol (Natarajan *et al.*, 1964) using a lead cathode is another reaction which is carried out without addition of any solvent. Saturation of the electrolyte with benzoic acid takes place rapidly by cathode rotation and the product benzyl alcohol which is a viscous liquid, is easily removed by the electrolyte from the cathode surface so that the process proceeds at very high efficiency. The effect of current density on current efficiency can be seen from Table IV.

TABLE IV

*Influence of current density on the current efficiency during the reduction of benzoic acid on a rotating lead cathode*

Catholyte	:	200ml of 10 per cent H <sub>2</sub> SO <sub>4</sub>
Benzoic acid	:	5g.
Temperature	:	80-90 °C
Anolyte	:	50ml of 10 per cent H <sub>2</sub> SO <sub>4</sub>
Current density (A/dm <sup>2</sup> )		Current efficiency (%)
10		92.8
20		91.4
30		93.0
40		93.2

A number of nitro compounds like *p*-nitro benzoic acid (Chidambaram *et al.*, 1970), *o*-nitro toluene (Chidambaram *et al.*, 1972) *m*-nitro benzene sulphonic acid (Thangavelu *et al.*, 1971) 3-nitro para cresol (Anantharaman *et al.*, 1970) *n*-nitroso-dimethyl amine, nitro guanidine (Balakrishnan *et al.*, 1971), *ortho*-nitrophenol (Anantharaman *et al.*, 1966) and *p*-nitrophenol (Udupa & Rao, 1967; and Swaminathan *et al.*, 1971) have been reduced using rotating cathode. In all these cases very high current density of the order of 20amp/dm<sup>2</sup> have been used which is not possible using a stationary cathode and employing stirring. The results are given in Table V. The possibility of using such high current densities enables the design of high amperage cells without substantial increase in the cell voltage.

In the reduction of glucose to sorbitol, the rate of reduction is dependent upon the concentration of glucose in the electrolyte. By employing the rotating amalgamated lead cathode, it is possible to achieve 90 per cent current efficiency when we reduce a solution containing 800gm/l glucose until the concentration goes down to 300g/l. If the stationary electrode is used, it is not possible to achieve such a high current efficiency.

In the oxidation of glucose to calcium gluconate (Sarada Menon *et al.*, 1954), using 2 per cent sodium bromide electrolyte, it has been shown that quantitative oxidation of glucose could be achieved by employing current densities upto

TABLE V  
Reduction of aromatic nitrocompounds to the corresponding amines

Sl. No.	Nitrocompound	Cathode (Rotating)	Reaction conditions		Products	Yield
			Medium	Temp. (°C)		
1	Nitrobenzene	Copper (disc)	Aq. 25 per cent H <sub>2</sub> SO <sub>4</sub> contg. 0.6 TiO <sub>2</sub>	40-50	25	Aniline 71
2	<i>o</i> -Nitrophenol	Copper (disc)	Aq. 10 per cent H <sub>2</sub> SO <sub>4</sub> contg. CuSO <sub>4</sub>	60-65	20-30	<i>o</i> -Aminophenol 82
3	<i>p</i> -Nitrophenol	Copper (disc)	Aq. 10 per cent H <sub>2</sub> SO <sub>4</sub>	50-60	15	<i>p</i> -Aminophenol 76(CE 85 per cent)
	-do-	Copper	Aq. 25 per cent H <sub>2</sub> SO <sub>4</sub> contg. 5-10 g TiO <sub>2</sub>	60-80		-do- 92(CE)
4	<i>o</i> -Nitrotoluene	Tinned copper (cylindrical)	Aq. HCl	40-45	10-20	<i>o</i> -Toluidine 86-90
5	<i>m</i> -Nitrotoluene	Copper (cylindrical)	Aq. 10 per cent H <sub>2</sub> SO <sub>4</sub> contg. 0.5 per cent CuSO <sub>4</sub>	70-80	2-20	<i>m</i> -Toluidine 80-86
6	<i>p</i> -Nitrotoluene	Tinned copper	Aq. 5 per cent HCl	35-40	10-30	<i>p</i> -Toluidine 75-80
7	<i>p</i> -Nitro benzoic acid	-do- (cylindrical)	Aq. HCl	65-70	10-20	<i>p</i> -Amino benzoic acid 90-95
8	3-Nitro <i>p</i> -cresol	Copper (disc)	Aq. H <sub>2</sub> SO <sub>4</sub>	50-55	10-20	3-Amino <i>p</i> -cresol 80-95
9	<i>m</i> -Nitrobenzene sulphonic acid	Copper (Cylinder)	Aq. H <sub>2</sub> SO <sub>4</sub>	30-40	2-12	Metanilic acid 57-70
10	<i>p</i> -Nitrophenetole	-do-	Aq. H <sub>2</sub> SO <sub>4</sub>	60-65	15-20	<i>p</i> -Phenetidine 70-75

20amp/dm<sup>2</sup>, without the current efficiency being affected. It was also observed that at high current densities, bromine loss would be also considerably minimised. This technique has been adopted in exploiting the process on a commercial scale.

### *Electro-Regenerated Redox Reagent*

The second technique of the use of electro-regenerated redox reagent for organic oxidation and reduction is a very important one from several points of view. This permits reactions being carried out under conditions similar to controlled potential conditions. In another paper to be presented here by my colleague (Pathy *et al.*, 1979), more details of systems are studied and the conditions of reaction will be covered, and as such it is not proposed to give more details here except to indicate the two systems which have been studied in detail and developed in :

1. Mn<sup>++</sup> — Mn<sup>+++</sup> system for oxidation of hydrocarbons (Venkatachalapathy *et al.*, 1960 & 1961; Ramaswamy *et al.*, 1963; and Chidambaram *et al.*, 1968) to aldehydes; and

2. Ti<sup>++++</sup> — Ti<sup>+++</sup> system for the reduction of nitro compounds (Anantharaman *et al.*, 1966) to the amino compounds in almost quantitative yields.

Mn<sup>+++</sup> is stable only in sulphuric acid of strength above 50 per cent and as such, this oxidation is carried out in sulphuric acid of such strength. Manganic sulphate formed by oxidation is insoluble in the sulphuric acid and since manganous sulphate is more soluble than manganic sulphate, the oxidation of manganous sulphate slurry was carried out so that a slurry of manganic sulphate could be obtained as the reagent. This reagent is used for oxidation of the hydrocarbon as an "out-cell" reaction. The manganous sulphate thus formed is recycled for regeneration of manganic sulphate in the cell and the process is continued.

Titanous sulphate is known to be a reagent used in the estimation of aromatic nitro compounds. The reduction reaction is very fast and in view of this it is possible to use this reagent for quantitative reduction of nitro compounds to amino compounds, in case we have a method of regenerating titanous sulphate as fast as it is used up. This was done by taking titanous sulphate in acid medium and regenerating titanous sulphate by cathodic reduction. The reduction of the nitro compound could be carried out as an "in cell" process. The amino compound formed is isolated as the amine sulphate and the acid made up and the electrolyte continuously used for reduction of further quantities of nitro compound. Where the reduction of the nitro compound to the amino compound is dependent upon the concentration of titanous sulphate, it is possible to carry out the reduction as an "out-cell" reaction. In this way, a number of nitro compounds (Udupa, 1978) have been reduced to the corresponding amino compounds in quantitative yields as given in Table VI.

### *Catalytic-Type Cathode*

For the reduction of certain types of organic compounds, use of catalytic type cathodes is known in electro-organic chemistry. The possibility of the reduction of

TABLE VI  
Reduction of nitrocompounds with  $Ti^{3+}/Ti^{4+}$  couple general experimental conditions

Catholyte	: 15-25 per cent $H_2SO_4$ containing 1 per cent titanic sulphate
Anolyte	: 15-25 per cent $H_2SO_4$
Cathode	: Stationary copper with stirring
Anode	: Lead
Current density	: 5-20 A/dm <sup>2</sup>
Temperature	: 45-80 °C
Cell voltage	: 3-4.5V
Diaphragm	: Ceramic porous pot

Sl. No.	Starting compound	Product	Cell current (amps)	Current efficiency (%)	Yield (%)	Energy Consumption (kWh/kg)
1	Nitrobenzene	Aniline	1000	83.8	97.0	12.4
2	<i>o</i> -Nitrophenol	<i>o</i> -Aminophenol	30	97.0	97.0	7.7
3	<i>p</i> -Nitrophenol	<i>p</i> -Aminophenol	1000	99.0	99.0	9.5
4	<i>p</i> -Nitrophenetole	<i>p</i> -Phenetidine	100	90.5	81.0	12.0
5	<i>m</i> -Dinitrobenzene	<i>m</i> -Phenylenediamine	30	98.7	99.0	18.7
6	2:4 Dinitrophenol	2:4 Diaminotoluene	30	85.0	97.0	18.6
7	<i>p</i> -Nitrochlorobenzene	<i>p</i> -Chloroaniline	20	82.6	98.2	7.3
8	<i>o</i> -Nitrotoluene	<i>o</i> -Toluidine	25	70.0	80.0	7.0
9	<i>p</i> -Nitrotoluene	<i>p</i> -Toluidine	150	80.0	90.0	5.5
10	<i>p</i> -Nitrobenzoic acid	<i>p</i> -Aminobenzoic acid	25	85.0	93.0	4.0

the nitrile group to primary amine ( $-\text{CN} \rightarrow \text{CM}_2\text{NH}_2$ ) is an important reaction. This can be carried out on palladium-black deposited cathode (Krishnan *et al.*, 1975). However, it was observed that palladium-black deposits on various metal substrates was not useful for this purpose and it was decided to try the use of carbon substrate as is done in catalysis. The possibility of depositing palladium-black deposit on graphite substrate was attempted and the use of the same as cathode in all reductions of nitriles was studied. This approach gave efficient reduction of the nitrile to the primary amine group. It was further observed that if palladium loss occurs, it could make the process uneconomical. As such, it was decided to try out catalytic type cathodes prepared by deposition of black nickel, black cobalt, and black iron on graphite substrates and use the same for the reduction of the organic nitrile (Krishnan *et al.*, 1976). The results obtained in the reduction of a number of nitrile-type of compounds are summarised in the Table VII given below (Udupa, 1978).

### *Oxide-Coated Anodes*

The possibility of depositing oxides of nickel and cobalt on different substrate materials like stainless steel, carbon and titanium have been carried out. The composition of such deposited oxide anodes have been investigated. The possibility of using such deposited anodes for the oxidation of organic compounds have been investigated. Since one of the communications (Trivedi *et al.*, 1979) by my colleague will be dealing with the topic in greater detail, it is not proposed to cover those details further. These oxide electrodes have the possibility of bringing about specific oxidations under well-defined experimental conditions. Oxidation of a number of alcohols have been studied using such anodes.

## ELECTRO-INORGANIC CHEMISTRY

### *Graphite Substrate Lead-Dioxide Anode*

The development of suitable types of anodes for carrying out inorganic chemical manufacture has been receiving the attention of electrochemists ever since electrochemicals are manufactured. In the manufacture of perchlorates, bromates, iodates and per-iodates, the anodes which are preferentially used are graphite, magnetite and platinum. Lead and its alloys have also been used. All these anodes have certain drawbacks when used in this process. In the manufacture of perchlorate, if platinum is used, the loss of platinum would be 6–10g/t of perchlorate produced. When graphite anode is used, in chlorate production, the loss of graphite could be approximately 15–25kg/t of chlorate produced. Apart from it, chlorate produced is contaminated with colloidal carbon which is difficult to remove from the chlorate produced. When magnetite is used as anode, the chlorate produced is contaminated with considerable quantities of ferric hydroxides and processing is cumbersome for the removal of the same in order to produce quality chlorate.

In the 1930s, Japanese workers found out the possibility of the use of electrolytically-deposited lead-dioxide as anode for the production of the above chemicals.



TABLE VII  
*Electroreduction of organic nitriles to primary amines*

Sl. No.	Nitrile used	Product obtained	Cathode material	Scale on which studied (amps)	Catholyte used	Yield efficiency (%)	C.E. (%)	Energy consumption (kWh/kg)
1	Benzonitrile	Benzylamine	(i) Deposited Pd Black	50	Ethanolic HCl	90	45	4.0
			(ii) Deposited Ni Black	75	Ethanolic H <sub>2</sub> SO <sub>4</sub>	65	36	16.3
2	Benzyl cyanide	Beta Phenyl-ethylamine	(i) Deposited Pd Black	50	Ethanolic HCl	85	40-45	6.7
			(ii) Deposited Ni Black	75	Ethanolic H <sub>2</sub> SO <sub>4</sub>	62	35	16.0
			(iii) Deposited Ni Black	500	Aq. ethanolic Am. sulphate	56	35	23.0
3	Mandelonitrile	1-Phenyl ethanalamine	(iv) Deposited Fe Black	10	Aq. ethanolic Am. sulphate	57	33	15.5
			(v) Deposited Co Black	10	Aq. ethanolic Am. sulphate	75	50	12.0
			(i) Deposited Pd Black	25	Aq. ethanolic HCl	76	38	6.0
			(ii) Deposited Ni Black	25	Aq. ethanolic Am. sulphate	60	40	13.0
			(i) Deposited Ni Black	20	Aq. HCl	80	40	16.0
4	Adiponitrile	Hexamethylene diamine dihydrochloride						
5	Dodecyl cyanide	Tridecylamine	(i) Deposited Pd Black	5	Ethanolic HCl	60	40	4.5
6	Cyano acetic acid	Beta-alanine hydrochloride	Deposited Pd Black	50	Aq. HCl	50	25	12.0
7	3-Cyanopyridine	3-amino methyl pyridine	Deposited Pd Black	8	Aq. HCl	50	25	8.25

Graphite is the substrate over which all the above depositions have been done

For nearly two decades, attempts were made to develop suitable size anodes for the use on a commercial scale. Several substrates like nickel and iron were employed and these substrates develop an oxide layer between the metal substrate and the deposited lead dioxide and it was not possible to use the anodes continuously. If the deposits crack, the substrate would introduce metallic impurities into the electrolyte which are not desirable. This was sought to be overcome by using platinum substrate, but this adds to the cost of manufacture of anodes. Massive lead dioxide anodes made by cutting with diamond cutters were adopted for making some of these chemicals. Making of ohmic contact on such massive anodes requires the use of silver foil or silver-conducting ink. So, satisfactory commercial anodes were not available till the 60s.

In our approach to this problem of making lead dioxide electrode, all these difficulties experienced by earlier workers were overcome by depositing lead dioxide on graphite substrate. This would permit the possibility of giving a solid support for the brittle lead dioxide which may be used in very thin layer on graphite itself. It also enabled the manufacture of electrodes of desired size and especially for use in high amperage cells for industrial scale production of the chemicals.

Lead dioxide is deposited from lead nitrate bath and the deposition of lead at the cathode is prevented by taking copper in the bath so that copper is deposited at the cathode. The liberation of acid as a result of deposition at the anode and cathode is sought to be neutralised by the addition of equimolar proportions of copper carbonate and lead carbonate to the bath during deposition. The formation of carbon dioxide bubbles at the anode surface would lead to pitting of the deposit and this is overcome by rotation of the graphite substrate so that the acid generated on the surface of the anode is dissipated into the bulk of the electrolyte and the reaction of the carbonate on the electrode surfaces is overcome and the bubbles of carbon dioxide adhering to the anode surface are also dislodged. Electrodes of different sizes suitable for commercial scale production have been made and the use of the same for the production of perchlorate, bromate, iodate and per-iodate studied. These are described in detail in another communication by my colleague (Narasimham & Udupa, 1979).

The use of graphite substrate lead dioxide anode for the production of chlorate has been studied in a 200amp cell which was later scaled up to 800amp cell and then to 5000amp cell. The cell-voltage remains constant in view of the fact that the inter-electrode distance remains constant and the product formed is free from any carbon particles. Several replacements of graphite electrode are overcome and the process economised.

These anodes are successfully employed for the oxidation of chlorate to perchlorate. Platinum has been successfully replaced by these anodes and the oxidation of sodium chloride to sodium perchlorate studied in 70amp cell and later scaled up to 400amp cell. The production of perchlorate normally involves two stages. The sodium chlorate is produced in a cell, using magnetite, graphite or graphite substrate lead dioxide anodes using a solution of sodium chloride containing dichromate as addition agent. The isolated sodium chlorate is used as electrolyte using a platinum

or graphite substrate lead dioxide anode for converting it into sodium perchlorate. Since lead dioxide anode could be used for the making of both chlorate and perchlorates, it was decided to use these anodes for the direct conversion of chloride to perchlorate in a single stage electrolysis. This has been achieved by avoiding the addition of dichromate by employing high current density for electrolysis using lead dioxide anodes. The current density used is of the order of  $15\text{amp}/\text{dm}^2$ , and the process has been run in a 5000amp cell and the electrodes have been found to have good life in the process.

Graphite substrate lead dioxide anodes have been used in the electrolytic process for making bromate. The bromate made by using graphite anodes normally has a light yellow colour and it is difficult to purify the product and make it colourless. However, the bromate produced using the graphite substrate lead dioxide anode is colourless and is pure. 500amp cell has been run for the process.

Similarly, these anodes have been used in the preparation of sodium iodate in a 500amp cell and sodium per-iodate for the manufacture of dialdehyde starch.

*Titanium Substrate Insoluble Anode (TSIA) (Udupa et al., 1972; and Thangappan et al., 1974)*

Chlor-alkali cells have been using graphite as anodes. The anode undergoes disintegration and graphite loss is of the order of 3–5kg/t of chlorine produced. As a result of the disintegration of the anode, the inter-electrode distance increases with the duration of electrolysis and the anodes are adjusted in mercury cells but in a diaphragm cell since there is no provision for adjusting inter-electrode distance, the cell-voltage increases with the duration of electrolysis. The graphite particles which are collected on mercury surface also lead to difficulties in the process and mercury loss is also there in the process. In order to ensure constant inter-electrode distance, attempts were made to use titanium substrate platinum anodes for caustic chlorine production. It was however soon realised, that though the initial investment is low, platinum consumption could not be controlled which added to the recurring cost to the product. The Beer patent in 1965 resulted in the development of titanium-substrate coated with precious metal oxides as anode, to replace the graphite anode in chloralkali cells. These anodes remain stable and the gas evolution on the same is favoured and the cell voltage is considerably lowered. There is a saving of the order of 10–15 per cent in the energy consumption per tonne of caustic soda produced in mercury cells. The purity of the chlorine gas is improved and it is free from carbon dioxide and hydrocarbons. Mercury loss is considerably decreased. In diaphragm cell, the life of the diaphragm itself is improved.

These anodes have been developed in this laboratory and they were tested in a diaphragm cell on a commercial scale as early as 1971 where its life was proved to be of the order of nearly 5 years at current density of  $2\text{--}3\text{kA}/\text{m}^2$ . These anodes were then installed in a 20kA mercury cell, where its life was proved to be more than  $1\frac{1}{2}$  years at a current density of  $5\text{kA}/\text{cm}^2$ . A number of plants in the country have put up experimental cells as given in Table VIII. The possibility of using these titanium substrate insoluble anodes for other processes is being investigated. The

TABLE VIII  
Comparative performance of TSIA in various chloralkali cells

Sl. No.	Name of the unit where TSIA are installed	No. of cells having TSIA	Rated Amperage (kA)	Current density (kA/m <sup>2</sup> )	No. of graphite anodes	No. of TSIA per Cell	Cell voltage with TSIA (v)	Average Cell voltage with graphite anode (v)	Saving in energy over graphite anodes (%)
<i>Mercury cells :</i>									
1	M/s. Hindustan Heavy Chemicals, Calcutta	24	20	4.0	40	40	3.9	4.4-4.5	11.3(min)
2	M/s. Dharangadhara Chemical Works, Sahapuram	15	65	3.2	174	174	3.8	4.4-4.5	13.6(min)
3	M/s. Gwalior Rayon, Nagda	4	160	8	72	72	4.0-4.1	4.6-4.7	13.0(min)
4	M/s. Century Chemicals, Bombay	2	50	5.0	50	50	4.0	4.5	12.0(min)
5	M/s. Nepa Paper Mills Ltd. Neapanagar	1	40	4.0	50	50	4.0	4.5	12.0(min)
6	M/s. Calico Chemicals, Bombay (Krebs cosmo)	1	50	5.0	50	50	3.9	4.5	13.0
7	Kanoria Chemicals, Renukoot (UP) (old cell)	2	50	5.0	50	50	4.1	4.6-4.7	11.0
	(new cell)	2	90	7.0	48	48	4.0	4.5	12.0
8	Standard Alkali, Bombay	3	120	6	72	72	4.2	4.7	11.0
9	Hukum Chand Jute Mills Ltd. Amlai	2	80	6	96	96	4.1	4.6-4.7	11
	<i>Diaphragm Cells :</i>								
10	Ballarpur Industries Ltd. Ballarpur	1	33	1.5	108	54	3.3	3.95	17
11	Tata Chemicals Ltd. Mithapur	2	10	1.0	90	30	3.0	3.7	18
12	DCM Chemicals, New Delhi (Trial)	2	1.2	0.8	24	6	3.5	4.0	14
13	Sirpur Paper Mills Ltd. Kagaznagar	2	1.5	0.8	24	12	3.2	3.8	16

possibilities of using them in metal winning and electroplating operations, their stability for organic oxidations are also being studied. Development of titanium substrate anodes with other metal oxide coatings is being vigorously pursued.

The existing cells in the country can be fitted with these metal anodes and can be operated at current densities 30-50 per cent higher than the present practice keeping the cell voltage the same, thereby leading to economy in the investment needed to changeover to metal anodes.

#### *Lead-Lead Dioxide Bi-Electrode (Narasimham & Udupa, 1977)*

The choice of a suitable anode for impressed current cathodic protection of installations in sea water is an important aspect to be looked into. Lead and its alloys have been used for this purpose. However, the surface of the anode gets passivated in the initial stages of its usage. This had been overcome by the development of a platinum-lead bi-electrode which was developed by Shrier (1961) who prepared the anodes by sticking in needles of platinum on the surface of lead-anode used in impressed current cathodic protection. When the surface of lead-anode gets passivated, the platinum needles help in passing of current which resulted in the formation of lead dioxide on the passivated surface close to the platinum needle which latter spread to the entire surface of the lead or its alloy anodes. The anode surface thus came to be covered with an adherent layer of lead dioxide which later helped in the cathodic protection by impressed current. Since we had developed graphite substrate, lead dioxide anodes as substitute for platinum for the production of perchlorate, it was decided that the lead dioxide would substitute platinum in the preparation of the bi-electrode also. Lead dioxide-Lead bi-electrode was thus prepared by sticking in a cylindrical piece of lead dioxide prepared from the massive lead-dioxide which had been deposited and which fallen off from the substrate. Such an electrode was studied for its behaviour with impressed current. Results similar to what has been achieved with the platinum-lead electrode can be achieved with such a bi-electrode of lead-lead dioxide. Such bi-electrodes can replace the platinum-lead bi-electrode and would be more economical and also effective for application of cathodic protection in sea water.

### SECONDARY METAL RECOVERY

#### *Direct Electro-Reduction of Metal Oxide etc. to Metal Powder*

Reduction of metal oxides/hydroxides to metal powder (zinc & cadmium) is carried out in a secondary battery during the charging of batteries. Such a technique which can be utilised for the manufacture of metal powders from by-product oxides and hydroxides has not been described in literature. In view of the fact that these metal oxides get reduced almost quantitatively when they are present on a cathode substrate, it was decided to employ this technique for preparing metal powders (Udupa, 1966; and Vijayavalli *et al.*, 1969) from by-product compounds for recycling metal powders in the process from which the by-products are obtained. Thus zinc oxide/hydroxide has been reduced to zinc powder from by-products

obtained in the hydro-sulphite industry and from organic chemical industry. Copper oxide obtained as a by-product from the utensil manufacturing units and from copper rod and wire drawing operations, has been reduced to copper powder. Millscale which is normally obtained to the extent of 6–8 per cent in the rod drawing and steel rolling operations has been reduced to iron powder (Warrier *et al.*, 1975*a, b*). Silver oxide can be reduced to extremely fine silver powder suitable for use in the manufacture of conducting ink (Udupa & Vasudeva Rao, 1965).

These processes have been studied on a laboratory scale and the scaled-up cells 500Å capacity and 3000Å capacity have been studied. Metal powders obtained in this manner can be recycled in the chemical industries and could also be used for powder metallurgy operations.

### *Suspension Electrolysis*

One other technique has been employed as a novel approach in metallurgy and relates to the possibility of recovery of metals from by-product oxides and hydroxides by suspension electrolysis. This technique can readily be employed for the recovery of secondary materials from various sources of raw materials. Zinc can be recovered (Alagusundaram *et al.*, 1975) from zinc oxide obtained as a by-product from the pigment industry, from chemical industry and from galvanising process. The suspension electrolysis can be carried out either in alkali or acid medium. Since zinc oxide is kept in suspension, the concentration of zinc in the electrolyte remains constant and zinc metal can be obtained in the form of a sheet on the cathode substrate from which the deposit can be removed and the metal obtained in the form of an ingot by remelting. Sulphuric acid is employed as the acid and the same generated at the anode, dissolves the zinc oxide kept in suspension and metal ion concentration is maintained constant during metal deposition. Normally, lead and its alloys are used as anode and it is necessary to ensure that the raw material used is free from harmful impurities, like chloride. The raw material which has been purified to make it free from chloride, can be used in the recovery of secondary metal. The process has been studied in a 1000amp scale cell and a number of plants have been commissioned for the recovery of secondary metals from various by-products.

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**Discussion**

V. S. BAGOTSKY (*The Institute of Electrochemistry of the Academy of Sciences of USSR, Moscow*): What is the Reynold number for the rotating electrodes in your cells?

H. V. K. UDUPA : It is in the range of turbulent flow.

A. V. GORODYSKY (*Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, USSR*): Were the black catalytic deposits dispersed metal or their oxides and hydroxides?

H. V. K. UDUPA : The nature of the deposit indicates that it is an oxide layer and not dispersed metal.