

Electrogenerative Systems

POTENTIAL USES INCLUDE CLEAN-UP OF FLUE GASES FROM COAL FIRED STATIONARY POWER PLANTS

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The concept of utilising favourable exothermic heats of overall reaction to produce chemicals while at the same time generating electrical energy in an electrochemical cell arrangement is appealing from an aesthetic viewpoint, and also responds to present day concerns about conservation and the environment. Some possibilities were noted by such eminent figures as Grove, the inventor of fuel cells in 1842 (1), and Nernst and others at the end of the nineteenth century (2). Yet, despite significant advances in electrochemical syntheses (3–6) and electrocatalysis since that time, the application of this electrogenerative approach to chemical processing has not progressed beyond research efforts in a few laboratories. Thus, many possibilities are not appreciated or have been overlooked. In this introductory discussion, which is intended for stimulation of further consideration, electrogenerative processing is explained and some means for its implementation are given, as are its limitations. Several types of systems also are described, as are some selectivity features, and possible ways for applying this approach to controlling nitrogen oxide and sulphur dioxide emissions.

More extensive discussion and pertinent references can be found in several reviews and recent articles (2, 6–12).

“Electrogenerative systems” or processes combine the favourable thermodynamics of overall reaction ($\Delta G < 0$) where the change in Gibbs' free energy should be negative, with mechanistic and kinetic factors to produce or remove a desired chemical, and to generate DC current between matched electrodes in an electrochemical cell arrangement. Fuel cell operations, which are related, generally emphasise energy production aspects in the cell and com-

plete oxidation (13, 14, 15). Electrogenerative systems share the use of catalytic electrodes and possibly even fuel cell components, but they differ significantly in that their main function is chemical processing with attendant considerations, and the electrical power is a by-product. The “electrogenerative” designation emphasises the chemical processing goals (6, 7, 9, 16). A consequence of this is that catalytic requirements at both electrodes may differ considerably from those of fuel cells.

With the long term view influenced by an interest in catalysis and the considerations above, a number of systems have been devised for performing selected electrochemical syntheses in a galvanic or “electrogenerative” mode (6, 7, 9, 12). Some electrogenerative systems of interest to this discussion are listed in the Table. While a variety of conventional and modified electrochemical methods can be used to study the pertinent half-cell electrode reactions (for example 17–19), in our laboratories overall electrogenerative systems generally have been investigated without any external power source and with simple controls. They incorporate two coupled electrode reactions, an appropriate barrier electrolyte, a provision for product recovery, and a circuit with a load for using the electrical energy, or possibly only to dissipate it, as illustrated by the system for studying electrogenerative hydrogenation in Figure 1. This approach insures feasibility and has stimulated continued improvement in current densities, components and cell configurations. Generally we have worked with aqueous solutions or aqueous compatible barrier electrolytes, such as some ion exchange membranes. Some other work on electrogenerative processes using solid electrolytes has been summarised recently by Vayenas (20),

and Stoukides (21), while Winnick and co-workers (22) have also discussed important related applications using solid electrolytes.

Some Electrogenative Systems and Their Characteristics

The hydrogenation of simple alkenes, conventionally a heterogeneous catalytic reduction, was utilised as an initial model system for investigating organic electrogenerative system operation (23, 24) and has been among the most extensively studied to-date. While the electrogenerative production of alkanes from alkenes is not a system of ordinary commercial interest, it is related to a number which are, and it has been useful for demonstration studies. Many approaches used in analysing electrogenerative alkene hydrogenation (for example the determination of rate expressions and mechanism) are applicable to other electrogenerative systems of the type described later. In this hydrogenation, hydrogen reacts across a barrier electrolyte phase bounded by porous, electrolyte-impermeable, catalytic electrodes. Figure 1 illustrates a cell design, together with associated circuitry, chosen from a number which have been used.

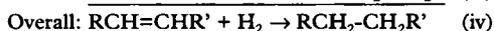
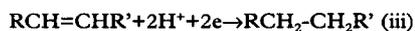
During operation, hydrogen ions which formed at the anode are transferred through the electrolyte, while electrons are conducted through the external circuit. Hydrogenation occurs at the counter, catalytic cathode (reducing electrode) at a controlled rate. With aqueous acid electrolyte, overall processes are:



Various Solution Transport Processes:



Cathode:



The open circuit cell potential is given by $E_{\text{cathode}} - E_{\text{anode}}$. For the hydrogenation of olefins, a characteristic reproducible open circuit voltage close to that calculated on the basis of free energy change (see the Table) is observed, although the olefinic electrode is not consid-

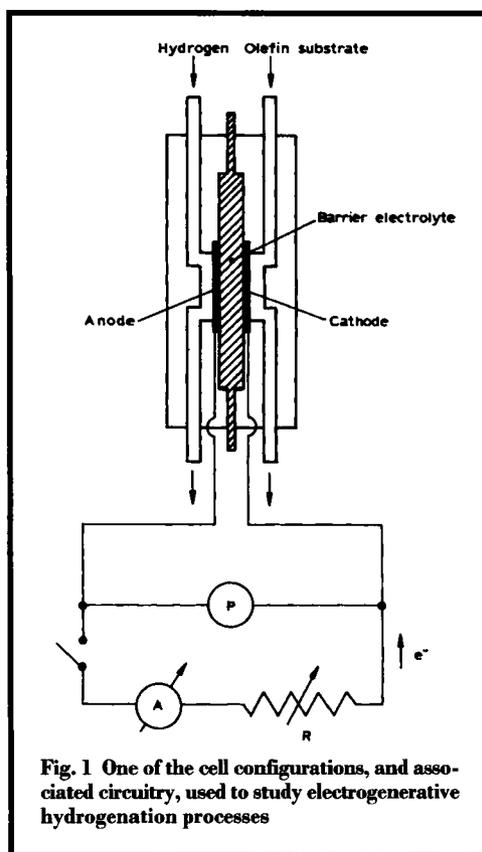


Fig. 1 One of the cell configurations, and associated circuitry, used to study electrogenerative hydrogenation processes

ered reversible. By varying the simple external load the rate (current) of reaction can be controlled. Electrode potential also varies because of polarisation. In this example, the low solubility of reactants and products in the barrier electrolyte limits any direct chemical reaction between hydrogen and the olefin reactants or "chemical shorting", so that the thermodynamic driving force is maintained. Reactions (i) and (iii) led to an overall reaction with an invariant electrolyte composition at significant current densities ($> 70 \text{ mA/cm}^2$) using high surface area, gas diffusion electrodes (23-25).

With constant ionic strength perchlorate electrolyte, the kinetics of ethylene electrogenerative hydrogenation at the cathode could be studied at liquid-impermeable, Teflon-bonded, platinum black American Cyanamid LAA-2 electrodes (9 mg Pt/cm^2) (25). Either the ethylene partial pressure or the concentration of the

Some Electrogenenerative Systems of Interest (6, 7)

Overall reaction	^a n	^c ΔH _R ^o kcal/mol	^d ΔG _R ^o kcal/mol	^e E ^o , V (calculated)	^f E, V (observed)
Reductions:					
C ₂ H ₄ +H ₂ →C ₂ H ₆	2	-32.7	-24.1	0.52	0.51
C ₆ H ₆ +3H ₂ →C ₆ H ₁₂	6	-49.3	-23.4	0.17	0.14
2NO _(g) +H ₂ →N ₂ O _(g) +H ₂ O _(l)	2	-70.4	-36.7	1.59	0.90
NO _(g) +1.5H ₂ +H ⁺ →NH ₂ OH·H ⁺ _(aq)	3	-52.3	-34.3	0.50	b
NO _(g) +2.5H ₂ +H ⁺ →NH ₄ ⁺ _(aq) +H ₂ O	5	-121.7	-96.4	0.84	b
Halogenations:					
C ₂ H ₄ +Cl ₂ →CH ₂ ClCH ₂ Cl	2	-52.2	-35.5	0.769	0.81
C ₂ H ₄ +Cl ₂ +H ₂ O→CH ₂ ClCH ₂ OH+HCl _(aq)	2	-46.7*	-35.6*	0.742	0.81
C ₂ H ₄ +Br ₂ →CH ₂ BrCH ₂ Br	2	-23.3*	-21.2*	0.460	0.61
Oxidations:					
C ₂ H ₅ OH+0.5O ₂ →CH ₃ CHO+H ₂ O	2	-51.8	-48.4	1.05	0.64
C ₂ H ₅ OH+O ₂ →CH ₃ COOH+H ₂ O	4	-128.5	-110.2	1.20	0.64
C ₂ H ₅ OH+3O ₂ →2CO ₂ +3H ₂ O	12	-336.8	-318.3	1.15	0.64
C ₄ H _{8(g)} +0.5O ₂ →C ₄ H ₈ O	2	-65.3	-53.3	1.16	b
SO _{2(g)} +0.5O ₂ +H ₂ O _(l) →H ₂ SO _{4(aq)}	2	-77.6	-48.8	1.06	0.65

^a Number of electrons involved
^b Not studied under requisite conditions
^c Change in enthalpy

* Estimated from group contributions
^d Change in Gibbs free energy at 298K
^e Standard e.m.f. ^f Open circuit

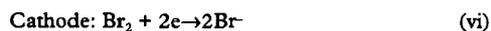
hydrogen ions was kept constant, at steady state positive potentials, while the other was varied under conditions where transport was not limiting. Thus, an order in each reactant at the cathode could be determined from:

$$\left(\frac{\delta \log i}{\delta \log C_i} \right)_{T,E,C_j} = Z_i \quad (\text{v})$$

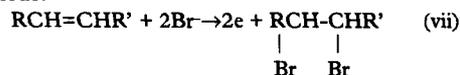
with the assumption of a simple exponential rate expression for the rate of reaction. Here, *i* is current density, *T* is temperature, *E* is potential, and *C_i* represents the concentration of a specific reactant at the electrode, *C_j* is the concentration of other reactants, and *Z_i* is the order of reaction with respect to any reactant. In recent years, more elaborate studies have been conducted on this hydrogenation reaction (26–28) for both platinum and palladium catalysts.

A variety of electrogenerative halogenation systems can also be operated to give dihaloalkanes and haloalcohols (6, 7, 16, 29) with olefins introduced at the anode. With electrogenerative bromination, for example, the overall elec-

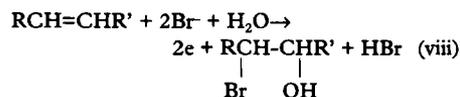
trode reactions with aqueous bromide electrolyte are:



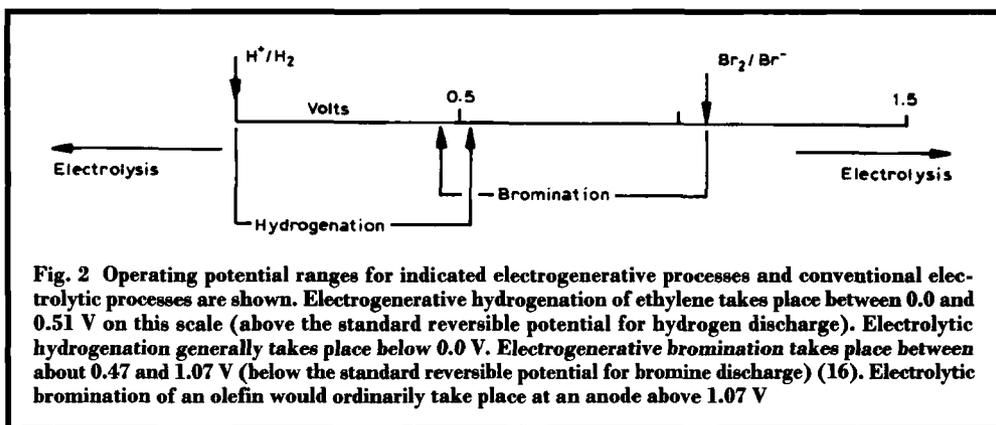
Anode:



or



When Reaction (viii) occurs the electrolyte is no longer invariant. One challenge is to control the system so that either Reaction (vii) or (viii) occurs selectively, since either bromohydrin or dibromoalkane can be the desired product. Control of selectivity, through potential or electrocatalysts at the anode, in order to favour either dihaloalkanes or haloalcohols has been described elsewhere for electrogenerative halogenations (16, 29). With a mixed reaction route available at the anode, as well as irreversibility, it is not surprising that the open circuit voltages for this system vary somewhat from those



calculated, as are shown in the Table.

The “potential windows” for the operation of cells for electrogenerative hydrogenation and bromination of ethylene are shown in Figure 2, together with the standard potentials of the reversible hydrogen and bromine electrodes, respectively. Potential regions on this scale where corresponding, energy consuming, electrolytic processes generally are operated are also indicated. It can be seen that the potential regions tend to be different. Electrogenerative hydrogenation occurs above the standard hydrogen reversible potential (~0 V) at positive voltages, while electrogenerative bromination occurs below the standard bromine/bromide reversible potential (~1.06 V) where bromide ion ordinarily would be discharged; see the caption discussion in Figure 2. Thus, for both types of reactions, the driving force for product formation in the electrogenerative mode contributes to ion discharge and the overall reaction at the electrode.

Nitric oxide, a gas of special interest from both basic and environmental considerations can also be reduced in the electrogenerative mode as a consequence of favourable thermodynamics ($\Delta G_r \ll 0$, see Table), in a cell similar to that shown as Figure 1. A polarisation or performance curve, A, corrected for ohmic loss in the electrolyte (IR correction), for the nitrogen oxide/hydrogen system at a moderate nitric oxide flow rate is shown in Figure 3; reaction conditions are indicated in the caption (30).

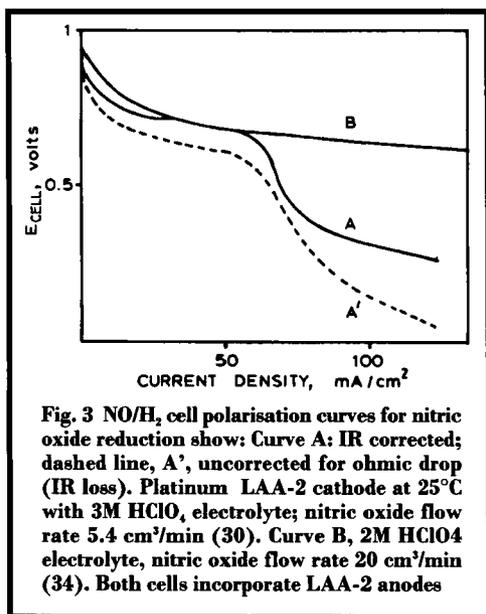
For comparison, the curve without IR correction is also presented in this Figure. The correction or voltage loss varies with current. Substantial currents of the order of 100 mA/cm² or higher are seen to be generated in the nitric oxide/hydrogen system with high surface area LAA-2 gas diffusion electrodes, which are gas permeable as well as electrolyte impermeable (31).

With the porous, catalytic electrodes, the following nitric oxide reactions can take place and have been observed under varying conditions:

Cathode:	E^0, V	
$2NO + 2H^+ + 2e \rightarrow N_2O + H_2O$	1.59	(ix)
$2NO + 4H^+ + 4e \rightarrow N_2 + 2H_2O$	1.6	(x)
$2NO + 6H^+ + 6e \rightarrow 2NH_2OH$	0.38	(xi)
$2NO + 10H^+ + 10e \rightarrow 2NH_3 + 2H_2O$	0.73	(xii)

where E^0 is the standard potential for these reactions. The hydrogen oxidation reaction at the platinum anode (Equation (i)) occurs fairly reversibly and readily, close to 0 V. Similar nitric oxide reduction products have been reported in a variety of heterogeneous catalytic studies. At the electrogenerative nitric oxide electrode, product selectivity is determined by kinetics and mechanism under the indicated cell conditions as well as by thermodynamics (17, 32, 33). Standard potential alone does not determine the course of the reaction.

The polarisation behaviour shown in Figure 3 can be interpreted in terms of two potential regions (30). From open circuit, 0.9, to 0.4 V

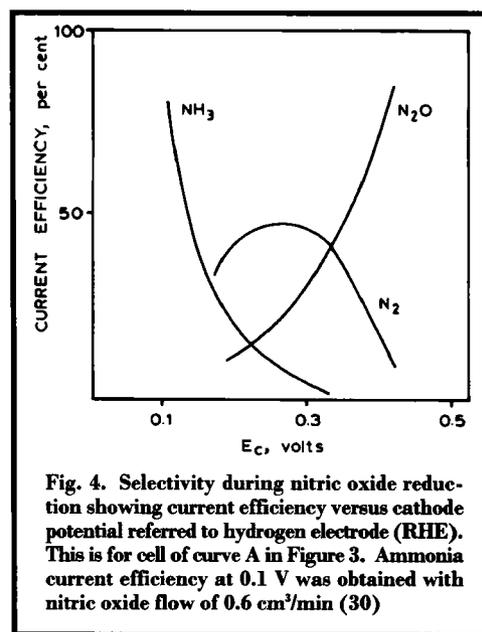


nitrous oxide (laughing gas) is the major product. The sharp potential drop with virtually no current increase corresponds to complete depletion of the entering nitric oxide stream (100 per cent conversion). Such limiting current behaviour can be observed with platinum electrocatalysts with relatively low nitric oxide flows, and corresponds to Reaction (ix).

For further selectivity analyses, current efficiencies (CE) can be considered. These are based on the calculated current for any product using the production rate and the number of electrons indicated in Equations (ix) to (xii) for the calculation, and dividing by the total measured current at a given potential (30, 34). The current efficiencies found in our laboratories (30) with perchlorate electrolyte are represented in Figure 4 as a function of the cathode potential referred to the reversible hydrogen electrode (RHE). Below 0.4 V the nitrous oxide current efficiency decreases sharply, while significant nitrogen formation begins; see Figure 4 and refer to Figure 3, (Curve A). The current efficiency for nitrogen formation, Reaction (x), goes through a maximum around 0.25 V. Ammonia formation also begins as nitrous oxide production drops off, at about 0.3 V. It is the

major product at potentials below 0.15 V. While some hydroxylamine is formed at potentials below 0.3 V, the current efficiency for its formation is not important (< 5 per cent) relative to other products under these conditions. However palladium, rhodium and ruthenium electrocatalysts all tend to promote more hydroxylamine formation (17). Both ammonia and hydroxylamine accumulate in the acid electrolyte while nitrogen and nitrous oxide exit in the cathode effluent.

Hydroxylamine is of special interest because it is relatively valuable, being used in the manufacture of caprolactam and aldoximes. Selectivity to hydroxylamine, Equation (xi), can be favoured by altering the conditions in a variety of ways (electrolyte, catalyst, etc.) (17, 34). By depositing sulphur in a controlled manner on the platinum catalyst, current efficiencies for hydroxylamine formation of ninety per cent or higher can be achieved (18, 33). These and other results suggest that there is the possibility of utilising an electrogenerative operation to produce hydroxylamine, as an alternative to the heterogeneous catalytic process (35). One special advantage of the electrogenerative option



is that both anode and cathode gaseous effluents can be recycled without any need for a separation stage.

The selectivity features of the nitric oxide/hydrogen system are illustrative of significant factors which can arise in electrogenerative processing, as compared with fuel cell operation. Besides selectivity, special problems include controlled catalysis and catalytic activity, as well as reactant and product recovery from processed streams. As can be seen from Figure 4, if attempts are made merely to maximise power or DC current generation without regard to desired chemical selectivity, cell operation might be shifted to unfavourable voltage ranges. The optimal conditions of operation also illustrate an important advantage for electrogenerative processing as compared with heterogeneous catalysis, in that the former offers the special possibility of controlling selectivity and rate through electrode potential, as well as through altering catalyst, surface structure and concentrations.

Currents in the nitric oxide/hydrogen cell can also be increased considerably through increased nitric oxide flow rate at the anode, in order to produce selectively nitrous oxide which is also of value. A polarisation curve for such a situation is shown as curve B in Figure 3. Of special interest is the fact that electrogenerative cells can be operated so that nitric oxide, in dilute gas mixtures, is reduced to a very low level (32–34, 36) suggesting a possible electrogenerative application to waste gas treatments.

Electrogenerative Processing of Potential Polluting Streams

Flue gas treatments or aspects of these treatments are among the most interesting potential applications for electrogenerative processes. Sulphur dioxide and nitrogen oxides present in the flue gas emitted from fossil fuel-fired power generators are recognised as the largest source of acid rain in the United States of America, and are very significant factors elsewhere. These atmospheric pollutants are also associated with other types of processing, such as nitric oxide and sulphuric acid manufacture, as well as with

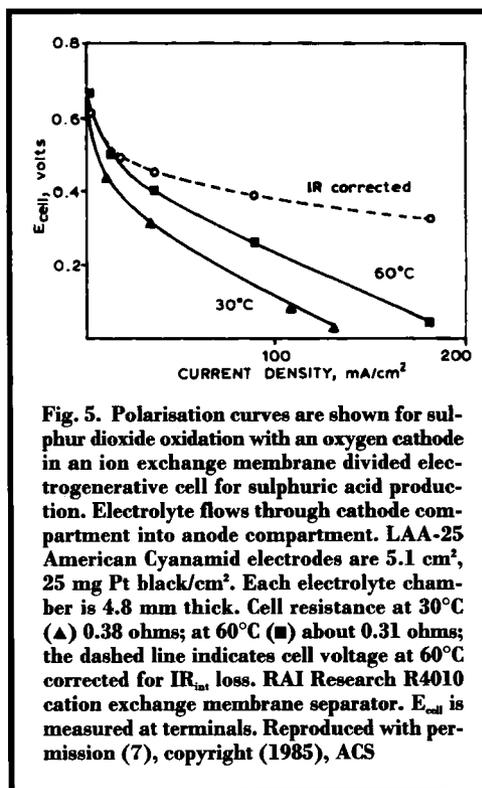
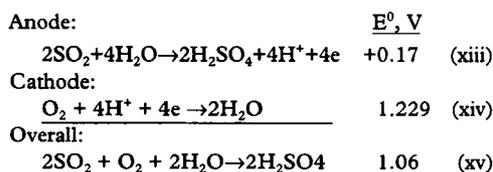


Fig. 5. Polarisation curves are shown for sulphur dioxide oxidation with an oxygen cathode in an ion exchange membrane divided electrogenerative cell for sulphuric acid production. Electrolyte flows through cathode compartment into anode compartment. LAA-25 American Cyanamid electrodes are 5.1 cm², 25 mg Pt black/cm². Each electrolyte chamber is 4.8 mm thick. Cell resistance at 30°C (▲) 0.38 ohms; at 60°C (■) about 0.31 ohms; the dashed line indicates cell voltage at 60°C corrected for IR_{int} loss. RAI Research R4010 cation exchange membrane separator. E_{cell} is measured at terminals. Reproduced with permission (7), copyright (1985), ACS

waste incineration and ore processing. Awareness of these problems continues to grow throughout the world. Electric utilities and industrial boilers were projected to emit 21 million tons of sulphur dioxide and 11 million tons of nitrogen oxides, accounting for 85 and 52 per cent, respectively, of these pollutant emissions during 1990 in the U.S.A. alone (37). A major portion of the sulphur dioxide emissions comes from older operations of modest capacity. With more coal-fired capacity coming on-line during the next decade, these types of operations may well be under pressure to achieve further emission reductions. In a comparison with conventional technology, electrochemical stages might well be more viable for modular, small-scale installation and so could emerge as better suited for these retrofit applications, as well as for some new uses. There was interest in electrochemical flue gas clean-up processes earlier (38, 39), but the high costs generally associated with them tended to discourage any

significant efforts. With electrogenerative processing, however, costs might be directed toward useful chemical production as well as to the elimination of pollutants. Earlier studies in our laboratories in connection with sulphuric acid production have shown that sulphur dioxide can be processed in electrogenerative cells at ambient temperature, and at 60–70°C, to give sulphuric acid and high currents (7,9) although both the sulphur dioxide and the oxygen electrodes operate about two-tenths of a volt away from standard potentials, even at open circuit. Cell performances with current densities approaching 200 mA/cm² are illustrated in Figure 5. The electrode reactions for sulphur dioxide oxidation can be represented as shown below (40).



A general electrochemical approach to the flue gas clean-up not involving an external power source can then be proposed (41, 42). One possibility, a modification of a standard approach, is shown in Figure 6. Particulates, sulphur dioxide and nitric oxide are all removed in separate stages. As we have seen, the pertinent electrogenerative reactions for flue gas clean-up have been demonstrated to be feasible separately at

high currents in preliminary reactor studies. These are sulphur dioxide oxidation to sulphuric acid, Equation (xv), and nitric oxide reduction to ammonia or hydroxylamine. Efforts for implementing these processes in clean-up would be in the direction of modifying them to meet performance criteria (including costs) for each stage, so that one or both types of reactors could be applied for low sulphur dioxide or nitric oxide concentrations. While platinum group catalysts in bulk form have been satisfactory for feasibility testing, catalysts supported on conductors such as carbon and in other configurations will be required for the future, because of economic considerations.

Dilute gaseous streams containing sulphur dioxide might be treated directly, or concentrating procedures such as the Bergbau-Forschung and Wellman-Lord or related processes might be applied to provide more concentrated gas streams or solutions for liquid phase processing (41, 42). Both commercial gas diffusion type anodes and packed bed electrodes have been studied for processing and removing low sulphur dioxide concentrations from gaseous and from liquid streams (42, 43, 44). The gaseous concentrations have approached those of common flue gases (43). These cited studies also can be reviewed as models for investigating other dilute gas streams for clean-up through electrogenerative processing. In connection with the investigation on electrogenerative processing of dilute sulphur dioxide in our laboratories, additional work

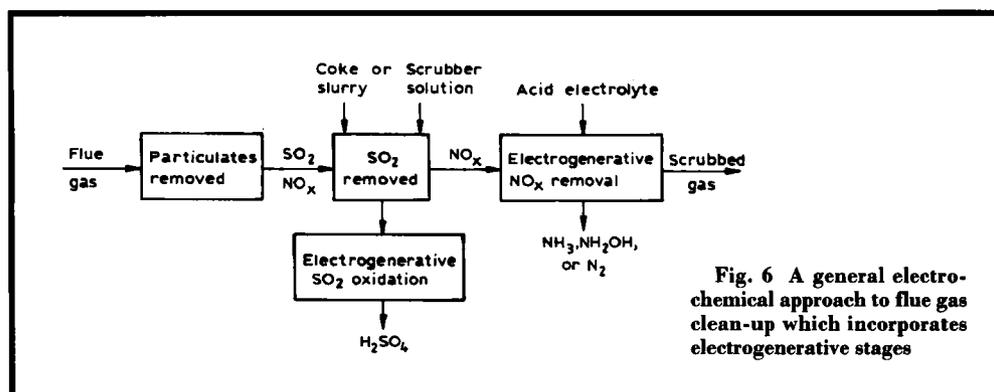


Fig. 6 A general electrochemical approach to flue gas clean-up which incorporates electrogenerative stages

was done on a pretreatment for anodic current enhancement through sulphur deposition onto an electrocatalyst via sulphur dioxide reduction. While some related treatments were used by other investigators earlier, little had been done on high surface area porous electrode treatments for reproducible, steady state use.

For dilute sulphur dioxide studies with gas diffusion electrodes (43), the design of the cell of Figure 1 was altered to provide a rectangular working anode configuration of 13×51 mm (6.45 cm^2 in area). Results for electrogenerative processing of 1 per cent sulphur dioxide in nitrogen are shown in Figure 7, for an LAA-2 electrode. Currents, of course, are well below those observed earlier with concentrated sulphur dioxide gas streams. However, relatively high conversions of 89 per cent and 55 per cent, depending on flow rate, could be achieved even with this small working area. Other data, more comparable to scaled-up cells, were obtained at higher flow rates. For scale-up, higher conversion could be achieved from longer flow paths and even several separate stages in series with anodes operating at different potentials, depending on clean-up and power generating strategy. Further investigation of commercial type gas diffusion electrodes obtained through Johnson Matthey showed that a gas diffusion electrode

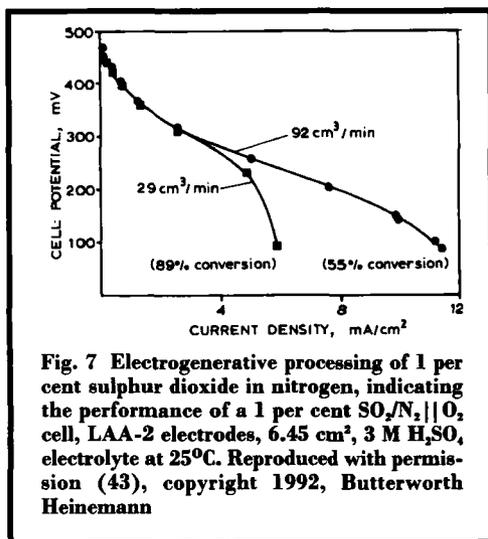


Fig. 7 Electrogenerative processing of 1 per cent sulphur dioxide in nitrogen, indicating the performance of a 1 per cent $\text{SO}_2/\text{N}_2||\text{O}_2$ cell, LAA-2 electrodes, 6.45 cm^2 , $3 \text{ M H}_2\text{SO}_4$ electrolyte at 25°C . Reproduced with permission (43), copyright 1992, Butterworth Heinemann

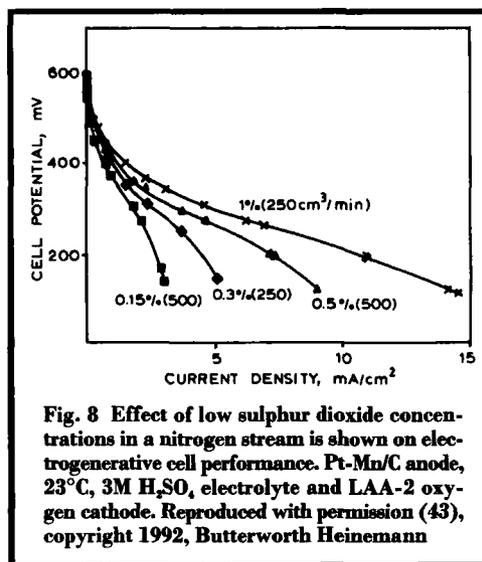
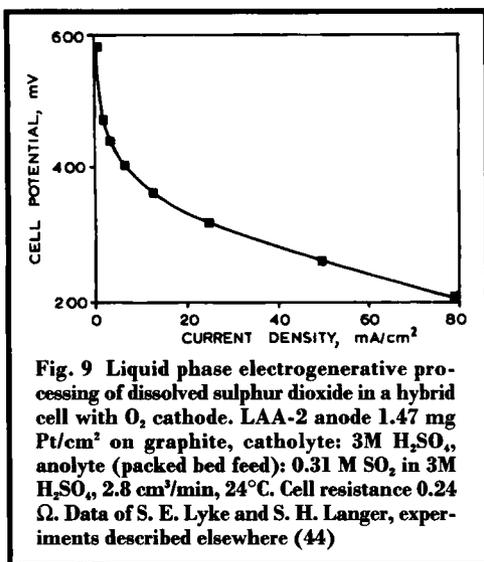


Fig. 8 Effect of low sulphur dioxide concentrations in a nitrogen stream is shown on electrogenerative cell performance. Pt-Mn/C anode, 23°C , $3 \text{ M H}_2\text{SO}_4$ electrolyte and LAA-2 oxygen cathode. Reproduced with permission (43), copyright 1992, Butterworth Heinemann

(NSX88/4/E1) incorporating carbon support, platinum (1.5 mg/cm^2) promoted with manganese, and a Teflon backing, would give an anode performance comparable to that of the more heavily loaded LAA-2 electrode which was used initially (43).

The effect on cell performance from lowering sulphur dioxide concentrations to levels close to those of effluent gas flow levels from power plants is illustrated in Figure 8. Differing high gas flow rates were used for various reasons but all were in substantial excess, so that the gas phase concentration was the critical factor in controlling the generated current. The important result is that electrogenerative operation is quite feasible at low concentrations and that these concentrations of sulphur dioxide can be reduced to still lower levels. Additional work has shown that even a three per cent oxygen concentration in a simulated 0.3 per cent sulphur dioxide effluent stream was not very deleterious to sulphur dioxide/oxygen cell performance when using a platinum-manganese/carbon anode and a high performance cathode with 3 molar sulphuric acid electrolyte (43).

An alternative strategy for processing sulphur dioxide from effluent gas streams is to anodically remove it from scrubbing liquors or solu-



tions resulting from concentrating procedures, such as those implied in the arrangement shown as Figure 6. With this in mind, oxidation of dissolved sulphur dioxide in liquid phase electrogenerative reactors with packed bed anodes also has been studied. In this feasibility investigation, platinum loadings in the range of 0.5 to 6 mg/cm² on porous graphite supports were emphasised (44). The hybrid type cell combined a gas diffusion cathode with the packed bed anode. Earlier work was done on both heavily loaded platinum anodes and graphite supported platinum (42), but the effects of a pretreatment protocol together with electrode preparation details were not quantified in many instances. Currents of 80 mA/cm² were generated though at room temperature with 0.5 M sulphur dioxide in 3 M sulphuric acid using a porous graphite anode sheet containing 18 mg/cm² of platinum and an efficient gas diffusion counter electrode in the hybrid cell and pretreatment. Further work showed that a loading decrease to 6 mg platinum/cm² could be attained with little sacrifice in performance.

Moving to lower loadings, it was found that with 1.5 mg platinum/cm² on the rectangular graphite sheet, packed bed anode (3 mm thick) in the hybrid cell, 55 per cent of entering 0.35 M sulphur dioxide in 3 M sulphuric acid elec-

trolyte flowing at 0.63 cm³/min, could be converted (44). A polarisation curve for a faster flow rate is shown in Figure 9. Significant currents of the order of 3 mA/cm² could be generated even at 0.003 M sulphur dioxide concentrations. For the future we must determine the extent to which increased platinum dispersion can be achieved with improved preparation methods to lower catalyst loading.

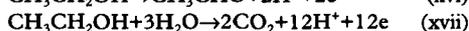
As already indicated, earlier work showed that nitric oxide reduction is very feasible in electrogenerative cells (34, 41, 45) and currents of 100 mA/cm² or higher are readily achieved. With more than 10 million tons of nitrogen oxides – originally mostly nitric oxide – produced in stationary power plants in the United States of America each year there are attractive possibilities for the recovery of this effluent component in chemical form; see Reactions (xi) and (xii). Furthermore, if nitric oxide can be removed economically through electrogenerative processing, power plant protocol, which is formulated so as to minimise its formation, might even be altered. Little work has been done with supported catalysts and dilute nitric oxide streams. However with LAA-2 type electrodes and some sulphur pretreatment it has been shown that electrogenerative nitric oxide conversions are particularly effective (33, 46). In studies with two to three per cent nitric oxide in various gaseous diluents, ninety to ninety five per cent conversions take place readily even in small scale laboratory cells with circular electrodes of the type in Figure 1.

Some questions regarding nitric oxide material balances remain for future consideration. The extent to which nitric oxide can be reduced to nitrogen (30, 47) has not been evaluated for dilute nitric oxide streams, and the maximum achievable concentrations of electrolyte soluble products must be determined. For flue gas clean-up applications, studies of operations with gas diffusion electrodes at low nitric oxide feed concentrations, for example 0.05 per cent, still must be undertaken. To process feed for cost effective current densities, that is, adequate nitric oxide removal rates, cells with special cathode gas channels may be required. Flow

across the face of the electrode should be controlled so as to assure lateral dispersion, while pressure drop must not be excessive. This type of problem, and others not discussed, are part of the challenge in future electrogenerative reactor design (48).

Additional Electrogenerative Possibilities

With growing interest in facets of biomass processing, alcohol oxidations to aldehydes or ketones become another area worthy of attention. Ethanol oxidation is of special interest particularly in the presence of water or water vapour. This is because the acetaldehyde product has a low boiling point (20.8°C) which facilitates subsequent separation where desired. In Figure 10, the rates of production of acetaldehyde and carbon dioxide from aqueous ethanolic vapour at a platinum anode, in a cell with an oxygen cathode, are compared (6). Their formation can be represented by Equations (xvi) and (xvii):



while at the cathode



Reaction (xvi) would be the desired one. In Figure 10, it can be seen that as the anode potential increases, acetaldehyde production also increases, reaching a maximum at about 0.68 V (versus RHE). At a higher voltage, the production of acetaldehyde then diminishes while undesired carbon dioxide formation, a desired fuel cell reaction, increases. Above about 0.73 V, catalyst activity deteriorates with time reflecting platinum oxide formation and catalyst deactivation (6). Thus, even though there is a pronounced increase in cell current with increasing potential, acetaldehyde selectivity considerations dictate the range and potential region of operation for this cell. It can be further noted that while an open circuit cell voltage of 1.05 can be calculated for standard conditions, as shown in the Table, the observed value is 0.64 V. Neither the ethanol anode nor the oxygen cathode ordinarily operate close to reversible

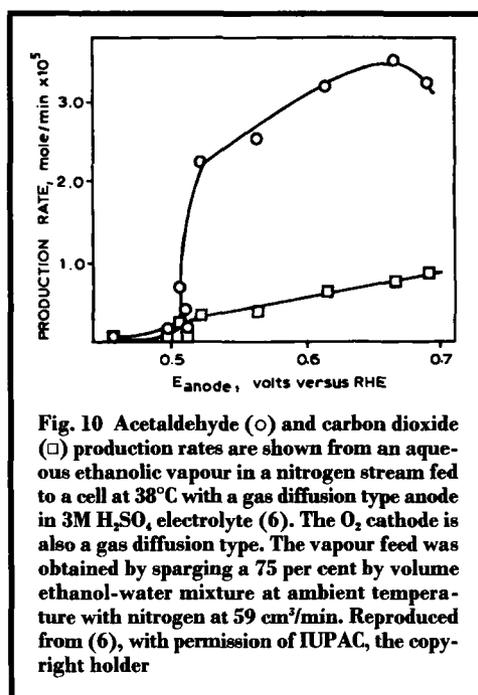


Fig. 10 Acetaldehyde (○) and carbon dioxide (□) production rates are shown from an aqueous ethanolic vapour in a nitrogen stream fed to a cell at 38°C with a gas diffusion type anode in 3M H₂SO₄ electrolyte (6). The O₂ cathode is also a gas diffusion type. The vapour feed was obtained by sparging a 75 per cent by volume ethanol-water mixture at ambient temperature with nitrogen at 59 cm³/min. Reproduced from (6), with permission of IUPAC, the copyright holder

potentials. Nevertheless, controlled electrogenerative conversion of ethanolic vapour to acetaldehyde seems feasible.

Stafford adapted fuel cell type components for a study of the electrogenerative oxidation of propylene at a palladium catalysed anode, using 25 per cent phosphoric acid electrolyte in the temperature range of ambient to 80°C (12). The interesting and special catalytic properties of palladium for allylic oxidation were demonstrated through the formation of acrolein and acrylic acid. Although selectivity was poor and currents were low in this pioneering effort, future improvements can be anticipated. Experiments with similar results to those of Stafford but with the catalysts deposited on solid polymer electrolytes have been reported more recently by Japanese workers (49). A number of related studies with solid polymer electrolytes have also been described (50).

Prospects for the Future

Electrogenerative systems differ from conventional electrolytic processing systems in that the need for an external power source can be

eliminated in many instances, thus providing advantages with respect to ease and scale of operation as well as capital investment. Even at the present stage of development, there is the promise that with minor refinements these cells can be developed advantageously to become standard laboratory devices since electrogenerative processing can be convenient while retaining many advantages of conventional electrolytic processing relative to heterogeneous catalysis. Among these are simple reaction rate control and special selectivity, as well as the capacity for operation under mild, controlled conditions. Views on costs and related factors in conventional electrochemical processing have been clouded by the uncertainty about future electric power costs and capital investment needs for equipment. However, when nine proposed electrochemical processes were thoroughly reviewed and analysed (3), the electrogenerative based preparation of methyl ethyl ketone from butene was one of two selected for potential future energy savings relative to corresponding chemical processes (51).

Limited work with electrogenerative and related systems to-date has also limited the recognition of their potential applications and their special features despite some recent activity in this direction (9, 10, 12, 49). While the types of processes studied in our laboratories have been emphasised here, other investigators, already cited, have emphasised solid electrolytes (20, 21) or catalytic electrodes supported on solid polymer electrolytes (49, 50). Interested readers may wish to consult the references provided here to work beyond the scope and breadth of this introductory discussion and identify addi-

tional candidate electrogenerative systems. Platinum and palladium have been the catalysts emphasised in work to-date but many possibilities exist for controlling selectivity with other metals and different approaches (17, 30, 46, 48). Electrogenerative type operations would seem to hold special promise for the future, even with modest electrochemical energy recovery. They might alleviate future energy needs while providing special advantages. With external electrochemical energy recovery, process cooling costs for highly exothermic reactions might be reduced (9). Basic research in this area also offers the promise of providing a link between heterogeneous gas phase catalytic systems and electrochemical syntheses (26, 27, 52). Further advances expected in the near future, should stimulate other workers and planners to give serious consideration to electrogenerative or related electrochemical routes in the processing industries.

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