

# Electrochemical hydrodimerization of formaldehyde to ethylene glycol\*

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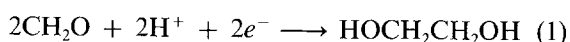
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The electrohydrodimerization of formaldehyde proceeds in close to quantitative yield and current efficiency to give ethylene glycol. The optimum process conditions require an aqueous formaldehyde solution of high concentration, a pH range of about 5 to 8, the presence of a quaternary ammonium salt, and reaction temperatures in excess of about 80°C. Remarkably, the process only works well at graphite, at which the enzyme-like specificity is believed to be related to the carbon surface oxide structure.

## 1. Introduction

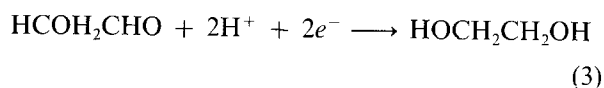
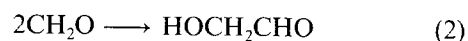
Presently all ethylene glycol (EG) is manufactured commercially via petroleum-based ethylene at the rate of about 9 billion kilograms annually worldwide. In this process, ethylene is converted to ethylene oxide in the presence of oxygen and a silver-based catalyst with a selectivity of about 80% and production of CO and CO<sub>2</sub> as byproducts. Hydrolysis of ethylene oxide results in EG. The major uses of EG are in antifreeze and in manufacture of polyesters, such as polyethylene terephthalate films, fibres and bottles. Many "C-1" routes, starting from syngas, methanol and formaldehyde have been proposed, and a number of these have been piloted over the years [1], but they are not practiced commercially because of unusually high pressures or catalyst problems. Should an electrochemical route to EG be commercialized, the process could be the third largest in volume after aluminum and chloralkali and could significantly lower dependency on petroleum.

An electrochemical route based on formaldehyde was first described by Tomilov *et al.* [2] in 1973. These workers electrolyzed an aqueous solution of formaldehyde at graphite electrodes at a pH of 2-5 using potassium dihydrogen phosphate as a supporting electrolyte and a mercury (II) catalyst. EG was reportedly formed at a current efficiency of 24.9%. This electrohydrodimerization process is analogous to the commercial electrochemical conversion of acrylonitrile to adiponitrile [3, 4], and is described as follows:



Watanabe and Saito [5] and Saito and Tokuyama [6] reported much improved current efficiencies (83%) using an aqueous alkaline solution of formaldehyde

at graphite cathodes at 50°C. Mercury salt was not required and an additional product, 1,2-propylene glycol, was found in low current efficiency. Weinberg and Chum [7] repeated the above work and discovered that mercury salt acts as a poison. Moreover, the presence of high methanol concentrations serves to suppress the process, while high concentrations of formaldehyde favor EG formation. One initial proposal was that glycolaldehyde, formed by condensation of formaldehyde, was reduced cathodically to EG:



However, no evidence of glycolaldehyde could be found using gas chromatography. An alternative mechanism involving the intermediacy of formaldehyde anion radicals could not explain the unusual requirement for graphite cathodes (only mercury has been found thus far to provide EG, but at low current efficiency [8], whereas all other metals and ceramic materials investigated are not electrocatalytic). Additional work [9] demonstrated the importance of pH control, catalysts and poisons; a mechanism was proposed based on the role of the electrode's carbon-oxide surface.

Subsequently, we studied the reaction variables in much greater detail and have published various aspects elsewhere [9-12]. This work demonstrated the importance of the cathode material, high concentration of formaldehyde, a less acidic pH range, high temperature and the presence of quaternary ammonium salt. Furthermore, an unusual mechanism was proposed in which the graphite cathode assumes

\* This paper is dedicated to Professor Dr Fritz Beck on the occasion of his 60th birthday.

"enzyme-like" behaviour. This report presents the first full publication, including results which have not previously been published, detailing the roles of the variables, the importance of poisons and other additives, current density, flowrate, etc. and providing further evidence in support of the original mechanism.

## 2. Experimental details

Reagent grade chemicals were employed "as received" including aqueous formalin (Eastman Kodak, 39.3% formaldehyde, 11% methanol, and 0.053% formic acid), low methanol grade formalin (DuPont, 39.0% formaldehyde, and 2.6% methanol), sodium formate (Fluka), quaternary ammonium salts (Southwestern Analytical), various inorganic salts and other chemicals. Carbon cathode materials were soaked in dilute aqueous acid (5% HCl or 5% H<sub>2</sub>SO<sub>4</sub>) for several hours, followed by washing in distilled water to remove metallic and other impurities.

Glass cell experiments were conducted with an ElectroSynthesis Company (ESC) Model 415 Potentiostatic Controller, Model 420X DC Power Unit and Model 640 Digital Coulometer. Larger scale flow cell studies used a Sorenson Model DCR60-45B power supply. An ESC Model 800 IR Measurement System was used for correction of electrode potentials. Single compartment and two compartment (ESC Model C-600) glass H-cells were provided with magnetic stirring, saturated calomel reference electrode (SCE), cathode (Ultra-carbon ST-50 rod) and platinum flag (10 cm<sup>2</sup>) anode. H-cells employed DuPont Nafion<sup>®</sup> 324 and 390 cation exchange membranes. Approximately 100 ml of formalin solution was used in each experiment. In H-cell and flow cell studies the anolyte was 10–20% by weight aqueous sulphuric acid. Glass cells were maintained at constant temperature by means of a water bath. Where sodium formate was used, the pH of the catholyte was maintained by addition of formic acid or sodium hydroxide as required.

Flow cell experiments were performed with an ElectroCell AB (Sweden) MP cell, typically fitted with Nafion 324 membrane, Union Carbide ATJ graphite cathode and platinized titanium anode assembled in a plate-and-frame manner with polypropylene frames and DuPont Viton<sup>®</sup> gaskets. The MP cell has a projected electrode area of 0.01 m<sup>2</sup>, an interelectrode gap of 12 mm and an electrolyte flow rate capability of 1–15 dm<sup>3</sup> min<sup>-1</sup> per cell. Figure 1 depicts the arrangement of the cell, pumps, flow meters, solution reservoirs and other equipment. Each compartment of the module was supplied with electrolyte solution from an electrolyte reservoir via a March (Model TE-MDX-MT3) explosion-proof magnetic drive pump, connected via polypropylene tubing. A glass condenser served as a heat exchanger in the anolyte loop. The reservoirs were constructed of 4 dm<sup>3</sup> heavy-wall, cylindrical, wide-mouth Nalgene<sup>®</sup> jars with screw cap lids. The catholyte reservoir lid had fittings for recirculating catholyte (about 2 dm<sup>3</sup>) from the cell and static loop return, vent, thermometer, gas (H<sub>2</sub>) sampling, liquid

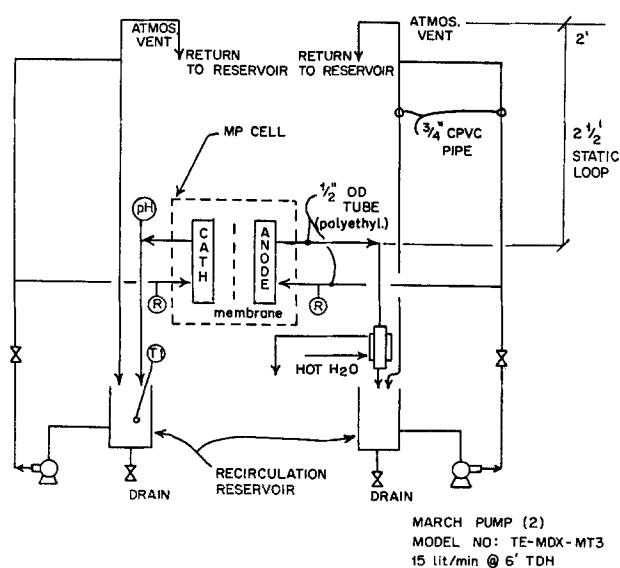


Fig. 1. Arrangement of cell piping, reservoirs, pumps, etc.

sampling, or pH adjustment. The anolyte reservoir had fittings for recirculating anolyte (about 2 dm<sup>3</sup>, 20% H<sub>2</sub>SO<sub>4</sub>) via the glass heat exchanger and static loop vent, thermometer, and gas outlet. A pH probe was inserted into the catholyte solution return line near the reservoir lid to facilitate monitoring and pH adjustment. Two SCE reference electrodes were inserted by means of fittings into the electrolyte inlets at the MP cell to monitor the cell voltage, electrode potentials and IR drop. All flow cell experiments were performed with continuous recirculation of electrolyte through the cell and reservoirs. Generally, electrolyses were conducted to the extent of about 2000 to 15 000 coulombs in glass cells and 1 to 3F in MP cell studies.

A Hewlett-Packard 7610A gas chromatograph with FID detector and Poropak Q column (2 m × 0.63 cm) served to analyze solutions for EG, 1,2-propylene glycol, glycerol and methanol, using 1,3-propanediol as an internal standard. Formaldehyde was determined according to the method described by Walker [13].

## 3. Results and discussion

The roles of the variables, including pH, temperature, concentrations of formaldehyde, methanol and EG, supporting electrolyte, current density, cathode materials and stirring/flowrate are described in the following.

### 3.1 Role of pH

Walker [13] has reviewed the role of pH on the chemical stability of formaldehyde solutions. At higher pH, the Cannizzaro Reaction occurs in which hydroxide ion causes the disproportionation of formaldehyde to methanol and formate (Equation 4), while at lower pH, acid catalyzed polymerization occurs (Equation 5).

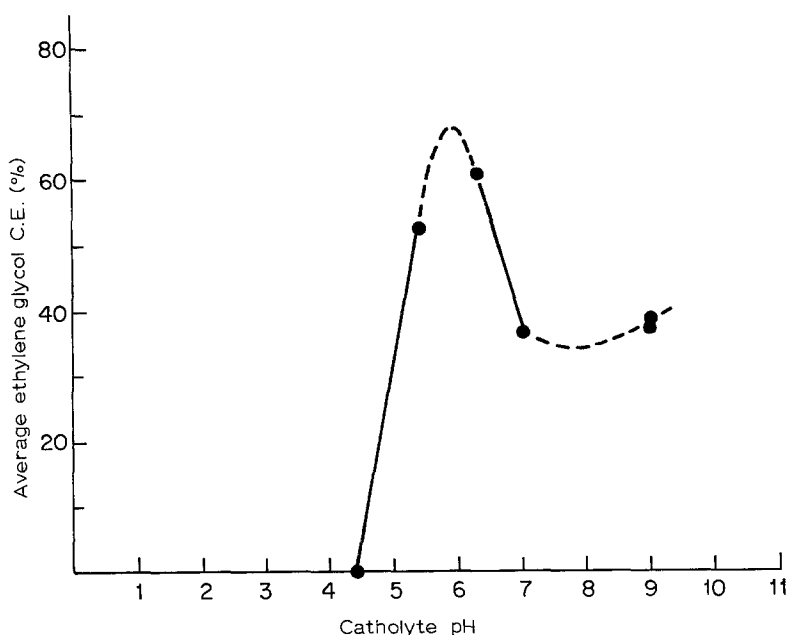
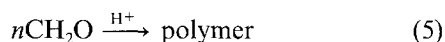


Fig. 2. Current efficiency against catholyte pH. Conditions: anolyte (18%  $\text{H}_2\text{SO}_4$ ), catholyte 3 M Na-formate in formalin; temp.  $60^\circ\text{C}$ ; no additives; current density  $100\text{ mA cm}^{-2}$ .

Thus,



The pH range for optimum storage stability of formaldehyde solutions is about 5 to 7, as is the optimum pH range for depolymerization. Fortuitously, the optimum pH range for electrohydrodimerization of formaldehyde lies within the range of optimum stability of formaldehyde.

Figure 2 plots current efficiency vs pH for a series of extended electrolyses under constant current conditions of  $100\text{ mA cm}^{-2}$  in the MP flow cell at  $60^\circ\text{C}$ , with no additives present in the aqueous formalin/sodium formate solution. The optimum pH range is about 5.5 to 6.5 and the current efficiency drops sharply at both lower and high pH's. We are unable to explain the results of Tomilov *et al.* [2] who studied the process at pH 2–5. We could not find EG under the reported conditions. In contrast, the procedures and results described by the Japanese workers [5, 6] were readily repeated; under the alkaline conditions, in which the pH was not controlled, the pH of the prepared solutions dropped rapidly from about 11 to about 8, even before electrolysis. Significant formate production therefore occurred (according to Equation 4) which served to neutralize the added base. Furthermore, we found that addition of quaternary ammonium salt and higher electrolysis temperatures caused the current efficiency maximum to reach nearly 100% in the optimum pH region.

### 3.2. The role of temperature

Higher temperatures are found to be beneficial in increasing the current efficiency for EG formation from less than 30% below  $40^\circ\text{C}$  to almost 100%, with added quaternary ammonium salt, at 80 to  $90^\circ\text{C}$ . Higher temperatures are known to increase the avail-

ability of free formaldehyde in solution [13] as well as providing the important additional benefits described below.

### 3.3. Role of concentrations of formaldehyde, methanol and EG

In earlier work [7] it was shown that the formaldehyde concentration in solution should be greater than about 20% by weight to achieve good current efficiencies of EG. Moreover, methanol was found to inhibit EG production, especially above about 20% by weight. These results and the requirement for higher temperatures are consistent with the need for free formaldehyde in unsolvated or hemiacetal form:



The equilibrium constant for this hydration is quoted as  $5.7 \times 10^{-4}$  at  $30^\circ\text{C}$  and  $3.0 \times 10^{-3}$  at  $64^\circ\text{C}$  [13], indicating that formaldehyde is almost entirely in the hemiacetal form as methylene glycol. Alcohols like methanol and EG can react with formaldehyde even more strongly than water. Therefore, the most efficient production of EG requires low methanol grades of formaldehyde, higher temperatures in order to maximize free formaldehyde, and EG concentrations in solution of no greater than about 15 to 20% by weight. This is illustrated in Fig. 3, where the use of a low methanol, high concentration (52%) formalin solution greatly extends the high current efficiency range to provide up to 23% EG product concentration. Some scatter was observed in the current efficiency values towards the latter stages of the experiment (Curve A) and this has been attributed to the difficulty in maintaining good temperature control and avoiding some evaporation losses of the more volatile 52% formalin solution.

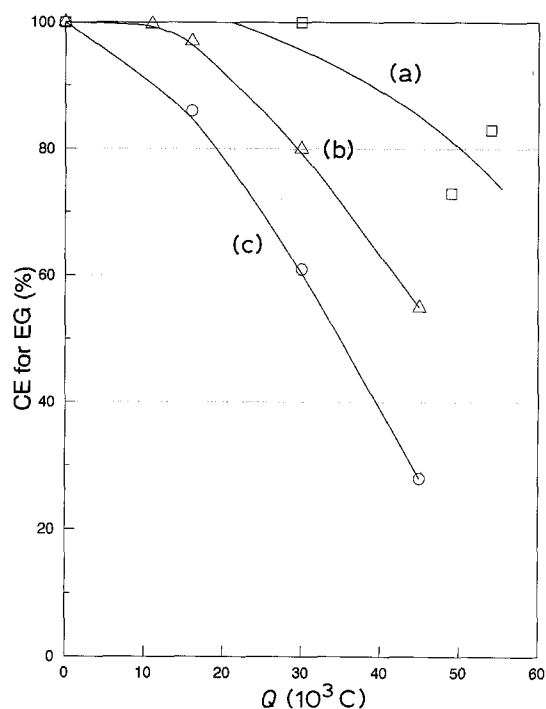


Fig. 3. Ethylene glycol current efficiency against charge for experiments performed in glass H-cells with Nafion<sup>R</sup> 324 membrane at 80°C with 1.0 M NaCOOH, 1% by weight (CH<sub>3</sub>)<sub>4</sub>NOH catholyte, 20% H<sub>2</sub>SO<sub>4</sub> anolyte, Ultracarbon ST-50 cathode, Pt anode. Curves: (a) 300 mA cm<sup>-2</sup> 52% CH<sub>2</sub>O, 2% CH<sub>3</sub>OH; (b) 200 mA cm<sup>-2</sup>, 39% CH<sub>2</sub>O, 10% CH<sub>3</sub>OH; and (c) 750 mA cm<sup>-2</sup>, 39% CH<sub>2</sub>O, 10% CH<sub>3</sub>OH.

### 3.4. Supporting electrolyte

Using a single compartment glass cell, fitted with graphite rod cathodes (Ultracarbon ST-50) and a platinum anode (10 cm<sup>2</sup>), a number of supporting electrolytes were screened in order to evaluate any unusual behavior of anions or cations in the process. Aqueous solutions of formalin at 55°C were electrolyzed at a cathode potential of -1.9 to -2.2 V/SCE with 1.0 M concentrations of (CH<sub>3</sub>)<sub>4</sub>NCl, NaCl, Na<sub>2</sub>SO<sub>4</sub> (0.2 M), sodium formate, lithium formate, ammonium formate, trimethylammonium formate, potassium formate, NaOH, KOAc and Na<sub>2</sub>HPO<sub>4</sub>. The pH of these solutions was maintained at 6.5-7.0. Current efficiencies were highest with the quaternary ammonium salt and lowest with ammonium and trimethylammonium formate. The others behaved almost equally. Moreover, a study of supporting

electrolyte concentration showed that the current efficiency for EG<sub>1</sub> formation was almost independent of concentration for sodium formate and potassium acetate. Sodium formate soon became the supporting electrolyte of choice for larger scale studies because of its low cost, availability, and good solubility and conductivity in formalin solutions.

Quaternary ammonium salts such as (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> and (nBu)<sub>4</sub>N<sup>+</sup> when present at about 0.5 to 2% by weight were found to increase the EG current efficiency significantly.

### 3.5. Poisons

Various chemicals were screened as potential poisons, including substances which could be present as a result of manufacture of starting materials as well as corrosion products from metallic reagent containers and piping. Table 1 presents results of electrolysis at 70-100 mA cm<sup>-2</sup> for seven additives examined in glass H cells with a catholyte of 100 cm<sup>3</sup> of 1.0 M sodium formate in formalin at pH 6.5-7.0 and 55-60°C. The anolyte was 20% aqueous H<sub>2</sub>SO<sub>4</sub>.

None of the additives had a significant positive effect on EG current efficiency, while the negative effect of Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and especially Cu<sup>2+</sup> are noteworthy. Further examination of Mg<sup>2+</sup>, Ca<sup>2+</sup> and Cu<sup>2+</sup> over a range of concentrations demonstrated that these ions become deleterious at concentrations as low as 0.1 M, 0.01 M and 0.0001 M, respectively. After electrolysis in the presence of Cu<sup>2+</sup>, a distinct layer of metallic copper could be seen on the cathode. The marked inhibition noted for Mg<sup>2+</sup> and Ca<sup>2+</sup> ions, unprecedented to our knowledge in electroorganic synthesis, is discussed in § 5.

The slight increase in current efficiency seen with EDTA was further examined under flow cell conditions at 100 mA cm<sup>-2</sup>, 60-65°C and at a pH of 6.5-7.0. Using 1.0 M sodium formate in formalin, a control experiment (no additive) gave a current efficiency for EG of 84%, whereas 1% by weight EDTA gave 86% and 1% ascorbic acid gave 90%. These small increases in current efficiency may be attributed to complexation of polyvalent metal ions which are present as impurities in the formalin solution, leached out of graphite electrodes, or resulting from other sources of contamination. Efficient production of EG requires scrupulous attention to impurity levels of polyvalent metal ions, ammonia and possibly primary, secondary and tertiary amines which could be present as byproducts in quaternary ammonium salts.

Table 1. Electrolysis of formalin solutions containing additives

Additive (conc)	Current efficiency (%) EG
EDTA (10 000 p.p.m.)	82
Control (no additive)	80
FeCl <sub>2</sub> (50 p.p.m.)	70
Pb(OAc) <sub>2</sub> (800 p.p.m.)	67
MgSO <sub>4</sub> (50 p.p.m.)	65
NH <sub>4</sub> OH (5200 p.p.m.)	64
CaCl <sub>2</sub> (50 p.p.m.)	56
CuCl <sub>2</sub> (800 p.p.m.)	0.0

### 3.6. Cathodic current density

Operation at high current density is a desirable objective for commercial operation in order to minimize capital costs. Using a single compartment glass cell, with a catholyte of 1.0 M sodium formate in formalin containing 1.0% by weight tetramethylammonium formate, at pH 6.5 and temperatures of 80 and 90°C,

Table 2. Role of cathodic current density

Current density (mA cm <sup>-2</sup> )	Charge (C)	Temperature (°C)	Current efficiency, EG (%)
100	6050	80	99
100	6789	90	90
200	12041	90	100
200	13350	90	90
400	15371	80	97
400*	15052	90	85
500	16625	80	96
500	15500	90	92
1000	7233	90	91

\* No quaternary salt was added.

a series of electrolyses were conducted over the range of current densities given in Table 2. Similarly, using the MP cell, electrolysis of 1.0 M sodium formate in formalin containing 0.6% by weight (*n*Bu)<sub>4</sub>NOH, pH 6.5–7.0, 400 mA cm<sup>-2</sup> and 82°C, gave a 97% current efficiency for EG upon passage of 3*F* of charge. Thus EG can be produced in current efficiencies of 90 to 100% even at relatively high current densities.

### 3.7. Cathode material

No other electrode material but graphite was found to give EG in high current efficiencies of up to 100%. Most of the metallic electrodes tested in undivided cells at 55–60°C in formalin solutions (1.0 M NaCOOH or 1.0 M KOAc) gave no EG. An exception is mercury which Montenegro *et al.* [8] discovered could give EG in about 25% current efficiency, probably via an organomercurial intermediate. The cathode materials which gave no EG include Pb, Cd, Sn, Zn, Al, Cu, stainless steel, carbon steel, Ni, V, Ag, Ebonex<sup>R</sup> (Ti<sub>4</sub>O<sub>7</sub>), Pt/Ir on Ti, tungsten carbide, and silicon carbide. Other carbons proved to be poorer in performance than graphite, including vitreous carbon (6%), reticulated vitreous carbon (23%), graphite cloth (2%), and a graphite fibre/epoxy resin composite (32%). Electrochemical preoxidation of graphite in 10% aqueous H<sub>2</sub>SO<sub>4</sub> generally raised the current efficiency. Even vitreous carbon gave EG in 17% current efficiency after preoxidation. Other experiments have shown that the current efficiency is also improved if graphite cathodes are first soaked in acid (such as HCl or H<sub>2</sub>SO<sub>4</sub>) for several hours to remove impurities, followed by thorough washing in distilled water.

### 3.8. Role of stirring/flow rate

Experiments were conducted using the glass H-cell containing a graphite rod cathode, Pt (10 cm<sup>2</sup>) anode, 1 M sodium formate and 2% by weight (CH<sub>3</sub>)<sub>4</sub>NOH in formalin at pH 6.5. The solution was maintained at 55°C and the catholyte was magnetically stirred. The current was monitored at a set cathode potential while the magnetic stirrer speed was varied over settings from 0 to its highest speed. At each fixed potential of

–1.6, –1.8 and –2.0 V/SCE (*IR* corrected) the current level remained fairly constant at (25 ± 3) mA, (83 ± 0.5) mA and (199 ± 2) mA, respectively. Flow cell studies likewise demonstrated that the rate of the reaction is independent of catholyte flow-rate over the range of 1–15 dm<sup>3</sup> min<sup>-1</sup> at constant cathode potential. Hence, electrohydrodimerization of formaldehyde is not mass transport controlled but is a kinetically controlled process under these conditions.

## 4. Current-potential studies

Attempts at cyclic voltammetric investigation using a graphite rod or a carbon fibre microelectrode mounted in glass were unsuccessful because of the high concentration of formaldehyde required for EG formation. Polarization curves (Fig. 4) of graphite rods (Ultra-carbon ST-50) at 55–60°C and pH 6.5 show that aqueous sodium formate is discharged at about –1.95 V and aqueous formalin at about –1.85 V/SCE, indicating a direct electron transfer process for formaldehyde. No limiting current for formaldehyde reduction was observed up to 1 A cm<sup>-2</sup>. Under these conditions a 70–80% current efficiency for EG was usually obtained on extended electrolysis. Tetrabutylammonium salt (2%) in formalin inhibits hydrogen evolution and raises the current efficiency for EG to about 80–90% at these temperatures under extended electrolysis, resulting in a polarization curve which lies more negative in potential to that with formalin above.

Tafel plots were constructed, using solutions of formaldehyde in the range of 0.012 to 12 M at 55°C at current densities of 0.01 to about 2 mA cm<sup>-2</sup> [12]. The Tafel slopes lie between 39–62 mV dec<sup>-1</sup> in the concentration range 0.012 to 0.20 M and change to slopes of 110–120 mV dec<sup>-1</sup> in the concentration range 1.2 to 12 M. This is consistent with the observation that EG is formed in relatively poor current efficiencies at concentrations below about 6 M, where hydrogen evol-

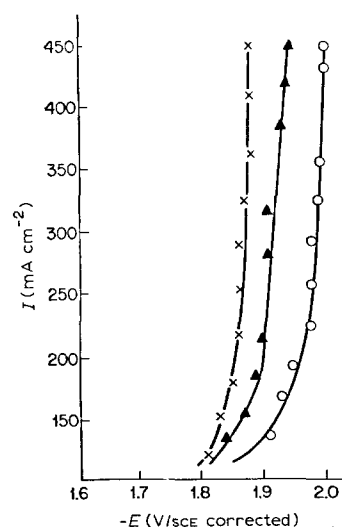


Fig. 4. Polarization curves for 1.0 M sodium formate in formalin at graphite. Temp. 55–60°C, pH 6.5. Key: (O) 1 M sodium formate in H<sub>2</sub>O; (x) 1 M sodium formate formalin; and (▲) 2% (*n*Bu)<sub>4</sub>NOH in 1 M sodium formate/formalin.

ution and perhaps methanol formation are the predominant processes.

The reaction order obtained from plots of log current density against log formaldehyde concentration was determined from the polarization data [12]. The slope (reaction order) was found to be fractional, approaching a value of 0.5 as the cathode potential was increased. The fractional reaction order suggests that formaldehyde or an intermediate species is adsorbed on the cathode prior to charge transfer, governed by Temkin adsorption [14].

### 5. Mechanism of EG formation

Attempts to study formaldehyde electrohydrodimerization by modern electroanalytical methods are made very difficult because the monomer concentration must be very high. This same situation exists in attempting to study the mechanism of electrohydrodimerization of acrylonitrile to adiponitrile [3, 4]. Interestingly, both processes occur at very negative potentials of about  $-1.9$  V/SCE and the Tafel plots show slopes of  $120$  mV dec $^{-1}$  [8, 12]. However, there are significant differences in these two processes, especially in appropriate cathode materials. The adiponitrile process can be conducted with many kinds of electrode materials including Cd, Hg, Pb, Pb amalgam, Zn, steel, Ti, Pt and graphite, with the higher hydrogen overpotential materials performing best. Also, whereas a mechanism involving the anion-radical of acrylonitrile reacting with acrylonitrile in a Michael addition best fits the observed results, a dimerization mechanism involving reaction of free formaldehyde anion radicals does not explain the unusual performance of graphite, and Hg, as the only metallic cathode. Moreover, a reasonable mechanism should also explain all the products, inhibition by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, the polarization data, and the roles of the reaction variables, including pH, temperature, stirring/flow rate, inhibition by methanol and EG at higher concentrations and additives.

We propose that a mechanism (Fig. 5) requiring prior dissociation of formaldehyde from its hemiacetal, condensation of free formaldehyde with carbon-oxygen functionality on graphite to give a new hemiacetal (A), and reaction of the latter with a second free formaldehyde upon electron transfer to give adduct (B), reasonably explains the experimental results to date. It is suggested that adduct (B) can undergo concerted intramolecular reaction and protonation to form EG and graphite oxide. Likewise, the small amounts of glycerol and 1,2-propylene glycol observed as byproducts could result from an adduct containing three formaldehydes such as (C).

Inhibition by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can be explained by blocking of important electrocatalytic carbon-oxide sites by chelation. In contrast, inhibition by methanol and ethylene glycol occurs by formation of formaldehyde hemiacetals of these alcohols which are more strongly associated than the hemiacetal of formaldehyde with water.

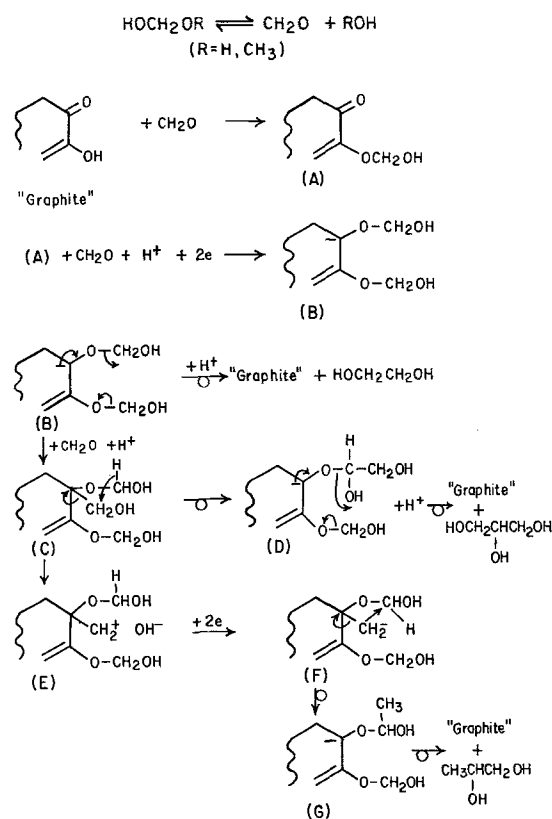


Fig. 5. Mechanisms for electrosynthesis of polyols.

Higher temperatures in excess of  $80^\circ\text{C}$  are beneficial in at least two respects to the kinetics: (i) more free formaldehyde is available for reaction; and (ii) promotion of carbon-carbon bond formation occurs in adducts like (B) and (C). Higher temperatures also serve to minimize hydrogen evolution and lower the cell voltage and hence the energy requirement.

### 6. Conclusion

At the time of writing two pilot studies are underway at two electrical utilities in Canada, Hydro Quebec and Ontario Hydro. If successful, they could demonstrate the commercial viability of the approach. What has been established thus far is that successful electroorganic processes need not be limited to higher value-added fine chemicals, but that commodity chemicals are also worthy of pursuit, providing the routes are technically sound, economically feasible and also possess other advantages such as improved environmental impact and ready availability of simpler, less expensive starting materials.

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