Electrooxidation of Urea at the Ruthenium Titanium Oxide Electrode

Urea adsorbs on the ruthenium titanium oxide electrode, depressing the observed current. For artificial kidney dialysate concentrations of urea and NaCl (0.50 kg/m^3 and 100 mol/m^3, respectively), the major electrolysis products are N_2, CO_2, O_2, and H_2, and the reaction mechanism is solution oxidation of urea by anodically generated active chlorine. A nitrogen-yielding direct electrode reaction is observed at high urea concentration (30 kg/m^3) and low NaCl concentration (10-100 mol/m^3).

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SCOPE

Urea is the major nitrogenous waste metabolite produced by the body. Bioengineering applications of urea oxidation by electrochemical means include water reclamation from urine for extended space flight (Lockheed, 1977), implantable bioelectrochemical sensors (Marincic et al., 1979), and dialysate regeneration for the artificial kidney (Yao et al., 1974; Bizot and Sausse, 1975; Fels, 1978). Previous investigations of urea electrooxidation have almost exclusively involved the use of platinum electrodes. Most investigators have claimed that the chloride in physiological solutions is first oxidized to active chlorine, and that urea is oxidized by the active chlorine in a bulk solution reaction (Bizot and Sausse, 1975; Lockheed, 1977; Fels, 1978; Quellhorst et al., 1978). However, urea adsorption on platinum electrodes has been confirmed by radiotracer experiments (Gromyko et al., 1979; Horanyi et al., 1979), and direct electrode reaction of urea has been reported (Gromyko et al., 1973, 1974; Keller et al., 1980).

High surface area ruthenium titanium oxide electrodes (Beer, 1966, 1967) provide a potential alternative to platinum electrodes. In the present study the electrochemistry of urea at the ruthenium titanium oxide electrode primarily was investigated for aqueous solution concentrations of urea and chloride found in artificial kidney dialysate; more concentrated solutions also were studied.

CONCLUSIONS AND SIGNIFICANCE

Urea (0.50-30.0 kg/m^3) depressed the observed anodic current, thus indicating urea adsorption on the ruthenium titanium oxide electrode. In the absence of a cell separator, electrolysis of solutions representative of artificial kidney dialysate (pH 7.5, 100 mol/m^3 NaCl + 0.5 kg/m^3 urea) above the chloride discharge potential yielded N_2 and CO_2 (from urea oxidation) and O_2 (from water oxidation) at the anode; H_2 is produced at the cathode. The N_2 evolved matched the urea consumed within experimental error (± 15%). Coulombic efficiencies for urea oxidation of 18 to 54% were observed. For these solutions, the mechanism for urea electrooxidation at the ruthenium titanium oxide electrode involves solution oxidation of the urea by anodically generated active chlorine in a series of reaction steps. The rate of the last overall step, which converts chlorinated nitrogen compounds to molecular nitrogen, increases with pH. At high urea concentrations (30 kg/m^3) and low NaCl concentrations (10-100 mol/m^3), a direct electrode reaction is observed that requires the presence of chloride but yields N_2. Since, for concentrations representative of artificial kidney dialysate,

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urea can be converted to N_2, CO_2, and H_2 with relatively high coulombic efficiency, electrochemical dialysate regeneration via ruthenium titanium oxide electrodes may be feasible, provided that the cell design incorporates zones at the appropriate pH for each of the major reaction steps.

Introduction

The present study is focused on the urea electrochemistry involved in the regeneration of artificial kidney dialysate. Electrochemical oxidation of urea, coupled with methods such as activated carbon adsorption to remove other waste metabolites, could constitute a system for regenerating spent dialysate for recycle. Spent dialysate typically contains approximately 0.3 kg/m^3 urea (5 mol/m^3) and 100 mol/m^3 of chloride. Previous investigations almost exclusively involved platinum electrodes. It has generally been reported that urea is oxidized by anodically generated active chlorine (Cl_2, HOCl, or OCl^-) (Bizot and Sausse, 1975; Lockheed, 1977; Fels, 1978; Quellhorst et al., 1978). The reactions for this mechanism (for convenience, active chlorine is shown as HOCl) are:

$$6Cl^- \rightarrow 3Cl_2 + 6e^- \quad (1)$$

$$3Cl_2 + 3H_2O \rightarrow 3HOCl + 3H^+ + 3Cl^- \quad (2)$$

$$3HOCl + H_2NCONH_2 \rightarrow N_2 + CO_2 + 3H^+ + 3Cl^- + 2H_2O \quad (3)$$

The direct electrode mechanism produces the same overall anodic reaction:

$$H_2NCONH_2 + H_2O \rightarrow N_2 + CO_2 + 6H^+ + 6e^- \quad (4)$$

For both mechanisms the cathodic reaction is hydrogen evolution. The overall reaction for the cell, for both mechanisms, is thus:

$$H_2NCONH_2 + H_2O \rightarrow N_2 + CO_2 + 3H_2 \quad (5)$$

For solutions dilute in NaCl and urea, the electrolysis of water can be expected as a side reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (6)$$

Previous studies of urea electrochemistry either tended to provide chemical data but were deficient in terms of detailed electrochemical measurements (the polarization curves in the Lockheed study were not corrected for IR losses), or presented electrochemical measurements but lacked the chemical data necessary to support mechanistic hypotheses (Gromyko et al., 1974). It is therefore difficult to reach a definitive conclusion regarding the conflicting reaction mechanism hypotheses.

Ruthenium titanium oxide electrodes consist of a metastable oxide film deposited on a titanium substrate (Beer, 1966, 1967). The mixed oxide films normally exhibit surface roughnesses on the order of 300 (Trasatti and O'Grady, 1981). These electrodes are used industrially to produce chlorine from concentrated chloride solutions, and chlorine evolution mechanisms generally postulate the existence of adsorbed elemental chlorine (Cl°_{ads}) on the electrode surface (Wright, 1982).

Ruthenium titanium tin oxide electrodes (RTTOE) were used in the present study. The addition of tin to the Ru/Ti oxide layer is reported to enhance electrode stability (Cook, 1975; O'Leary, 1975). These electrodes can be fabricated in a number of interesting geometries, including porous, flow-through electrodes. The present study was directed at developing the basic knowledge of urea electrochemistry at the RTTOE required for the design of an advanced dialysate regeneration system (Michaels et al., 1984). The objectives were:

1. To determine the mechanism of urea electrooxidation at the RTTOE for urea and chloride levels representative of spent dialysate.
2. To elucidate, in so far as possible, the detailed chemistry of the reaction.
3. To test the reaction mechanism theory in more concentrated urea and chloride solutions.
4. To formulate an initial assessment of the feasibility of regenerating dialysate by urea removal via electrooxidation at the RTTOE.

In most experiments urea concentrations of 0.50 kg/m^3 were employed in order to cover the maximum concentration range likely to be encountered in spent dialysate.

Experimental

Electrochemical apparatus

A schematic diagram of the experimental system is shown in Figure 1. The working electrode(s) consisted of a 21 cm^2 flat titanium plate ruthenized by four coats of a mixture of $RuCl_3$, $SnCl_2$, and tetra-*n*-butyl titanate in *n*-butyl alcohol fired at 440–470°C. The RuO_2:SnO_2:TiO_2 ratio was 0.19:0.13:0.68. The back side of the electrode(s) was masked with Teflon adhesive tape. The counterelectrode was a platinum mesh screen separated from the RTTOE by 6 mm. Potential was measured via a saturated calomel electrode (SCE) placed in a Luggin capillary. Potential was controlled via a Princeton Applied Research model 371 potentiostat, and measured potentials were corrected for IR losses by the current-interrupt technique (McIntyre and Peck, 1970; Kuhn and Mortimer, 1973). A Nafion 425 cell separator was installed between the electrodes in some experiments. The cell itself was an enclosed Plexiglas cylinder of 3.3×10^{-4} m^3 volume.

A magnetic stirring bar was located behind the working electrode to provide convection. Additional solution circulation could be provided by two Teflon tubes connected to the tubing pump and reservoir flask. The tubes were positioned on the working electrode front surface. At current densities greater than approximately 3 mA/cm^2, the electrode was so strongly polarized that circulation through the tubes did not affect the polarization curves. The cell top plate also contained ports (not shown in Figure 1) for gas flushing and sampling. A port was provided in the cell bottom for solution sampling. Experimentation was carried out with two RTTOE's, both produced in the same coating run.

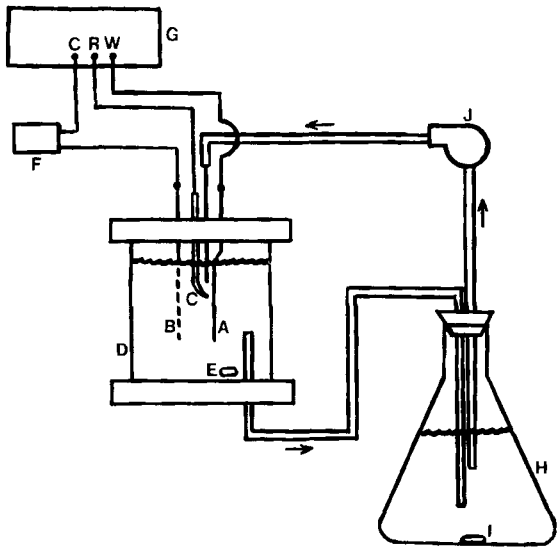


Figure 1. Diagram of electrochemical system.

A. Ruthenium titanium oxide electrode
B. Platinum mesh counter electrode
C. Luggin capillary
D. Plexiglas cylinder
E. Stir bar
F. Mercury wetted relay
G. Potentiostat
H. Reservoir flask
I. Stir bar
J. Tubing pump

Solutions and analytical methods

Solutions were prepared from reagent grade chemicals and purified distilled water (Mill-Q System, Millipore Corp.). The phosphate buffer (pH 7.5) concentration was $[H_2PO_4^-] = 1.6$ mol/m^3 and $[HPO_4^{2-}] = 8.5$ mol/m^3. Urea concentrations were measured by the diacetyl monoxime assay (Sigma, 1974). Residual chlorine was determined by titration with potassium iodide and measurement of the resulting iodine concentration via an iodine sensing electrode (Orion Model 97-70; Kolthoff and Belcher, 1957; APHA, 1975; Orion Research, 1977; Rigdon et al., 1978; ASTM, 1979). Residual chlorine was defined as the sum of nitrogen-bonded chlorine and active chlorine [Cl_2(aq), OCl^-, HOCl]. Monochlorourea was identified by its UV absorption maximum at approximately 244 nm, and what was presumed to be N,N'-dichlorourea was identified by a UV spectrum monotonically declining with increasing wavelength (Colton et al., 1954; Wright, 1982). Product gas compositions were determined by using a Hewlett Packard 5830A gas chromatograph containing columns of either porous activated carbon (Carbosieve S) or molecular sieve 5A. Measurement of pH was accomplished with a glass electrode.

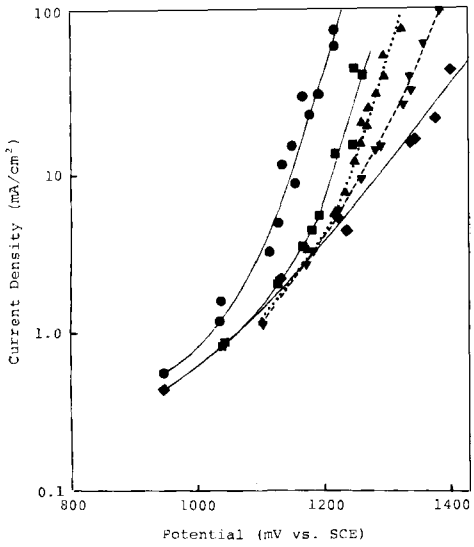


Figure 2. Effect of urea on polarization curve for 100 mol/m^3 NaCl + pH 7.5 phosphate buffer.

● no urea; ■ 0.50 kg/m^3 urea; ▲ 2 kg/m^3 urea; ▼ 5 kg/m^3 urea; ◆ 30 kg/m^3 urea.

Procedures

Steady-state anodic polarization curves were taken in the direction of increasing potential. The pump and reservoir flask were used in the polarization experiments. Batch electrolysis experiments were performed in either the potentiostatic or galvanostatic mode. Cell connections to the pump and reservoir flask were clamped off during batch electrolysis experiments.

Chemical oxidation experiments

Using a syringe pump, active chlorine solutions (50 to 100 mol/m^3 in active chlorine) were injected at a fixed rate into a reaction vessel containing 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solution. The injection rate was approximately equal to calculated rates of chlorine generation in the electrochemical experiments. Reaction vessel volume was 4.0×10^{-4} m^3, and the vessel contained ports for gas flushing as well as gas and solution sampling. Urea solutions were buffered to pH's of 4.5, 7.5, and 9.9. Analytical procedures were as described above.

Results

Polarization behavior

Steady-state anodic polarization curves are presented in Figure 2 for pH 7.5 phosphate-buffered 100 mol/m^3 NaCl solutions. Urea, at all concentrations studied, depressed the observed current density relative to the urea-free solution.

For the urea-free 100 mol/m^3 NaCl solution shown in Figure 2, the slope of the polarization curve (Tafel slope) is 82 ± 12 mV/decade at current densities greater than approximately 3 mA/cm^2. The presence of urea at the 0.50 kg/m^3 level and at the 2.0 kg/m^3 level did not alter the Tafel slope. Urea concentrations of 5.0 and 30.0 kg/m^3 increased the Tafel slope.

In the 100 mol/m^3 NaCl and the 0.50 kg/m^3 urea + 100 mol/m^3 NaCl solutions, the presence of the Nafion separator did not affect the polarization curves. However, although the electrolyte was buffered to pH 7.5, the pH in the anode compartment of the cell with the Nafion separator dropped to pH 2. This pH decrease was due to the simultaneous oxidation of water in the dilute chloride and urea solutions under study. In the absence of the separator, the observed pH range for the phosphate buffered solutions was 7.2–8.5.

The effect of urea on polarization behavior in 100 mol/m^3 Na_2SO_4 solutions is shown in Figure 3. Urea depressed the observed current. In Figure 3 the anodic Tafel slope in urea-free sulfate solution is 92 mV, which is identical (within experimental error) to the Tafel slope in urea-free 100 mol/m^3 NaCl. In contrast to the behavior in 100 mol/m^3 NaCl solutions, 0.50 kg/

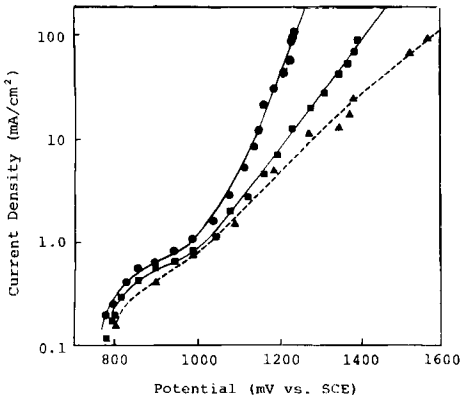


Figure 3. Effect of urea on polarization curve for 100 mol/m³ Na_2SO_4 + pH 7.5 phosphate buffer.

● no urea, no separator; ■ 0.50 kg/m³ urea, no separator; ▲ 30 kg/m³ urea, Nafion separator installed.

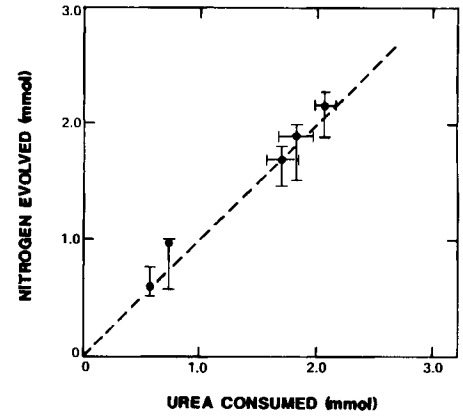


Figure 5. Nitrogen/urea balance in electrolysis of pH 7.5 phosphate-buffered 100 mol/m³ NaCl + 0.50 kg/m³ urea in the absence of a cell separator.

m³ urea increased the anodic Tafel slope to 180 mV/decade in 100 mol/m³ Na_2SO_4 solutions. An even greater increase in Tafel slope was produced with 30 kg/m³ urea. The polarization curves for 30 kg/m³ urea + 100 mol/m³ Na_2SO_4 and 30 kg/m³ urea + 100 mol/m³ NaCl essentially are identical up to 1,350 mV vs. SCE.

Polarization curves in unbuffered 2,000 mol/m³ NaCl solutions are shown in Figure 4. For the urea-free 2,000 mol/m³ NaCl solution, the Tafel slope ($i \geq 10$ mA/cm²) is 28 mV/decade, which is consistent with values reported elsewhere (Krishtalik, 1981; Wright, 1982). For the 2,000 mol/m³ NaCl solutions, the presence of urea depressed the observed current densities at current densities greater than approximately 3 mA/cm².

Mass and coulombic balances

Nitrogen (from urea oxidation), oxygen (from water oxidation), and hydrogen (from cathodic reduction of water) were found to be the major gaseous products from electrolysis of pH 7.5 phosphate-buffered 100 mol/m³ NaCl + 0.50 kg/m³ urea solutions. Carbon dioxide (from urea oxidation) was also observed in the gaseous products of electrolysis, but in lower quantity than the other products, due to the high solubility of carbon dioxide in water. Figure 5 compares the urea consumed with the nitrogen evolved for electrolysis in the absence of a cell separator. The nitrogen evolved was equal to the urea consumed within an experimental error of ±15%.

For 100 mol/m³ NaCl + 0.50 kg/m³ urea solutions in the absence of the cell separator, the measured charge (Q_{act}) was compared with the equivalent charge (Q_{equiv}) for the observed electrooxidation products. Q_{equiv} was calculated from:

$$Q_{equiv} = Q_{N_2} + Q_{O_2} + Q_{resid\ Cl} \tag{7}$$

Q_{equiv} was found to equal Q_{act} within an experimental error of ±12%; therefore, coulombic balance is observed.

Effect of current density and electrolyte composition

For 1.0 kg/m³ urea solutions, Figure 6 presents data on the variation of the relative ratio of nitrogen to oxygen with current density in the absence of the cell separator. (A urea concentration greater than 0.50 kg/m³ was required in these experiments

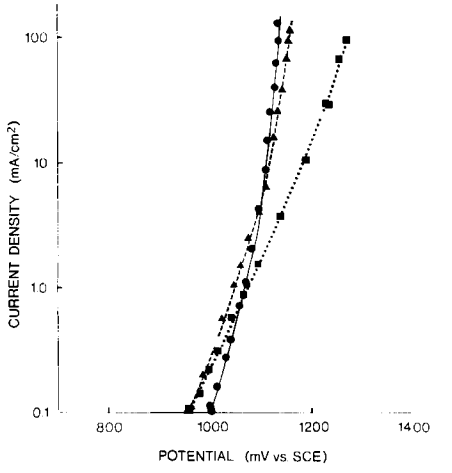


Figure 4. Effect of urea on polarization curve for unbuffered 2,000 mol/m³ NaCl.

● no urea; ▲ 0.50 kg/m³ urea; ■ 30 kg/m³ urea.

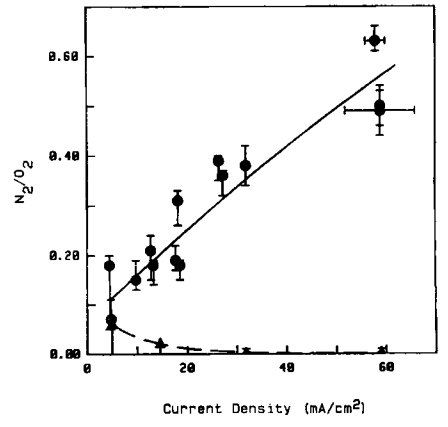


Figure 6. Nitrogen/oxygen ratio in product gas from electrolysis of pH 7.5 phosphate-buffered 1.0 kg/m³ urea solutions in the absence of a cell separator.

● 100 mol/m³ NaCl; ▲ 100 mol/m³ Na_2SO_4.

due to the high rate of urea oxidation at higher current densities.) For the 100 mol/m^3 NaCl-containing urea solutions, the relative amount of nitrogen that was evolved increased with current density. Compared to these solutions, there was minimal nitrogen evolution from urea solutions containing 100 mol/m^3 Na_2SO_4 as the electrolyte. Measurement of the urea concentration yielded coulombic efficiencies for urea oxidation of less than 10% for the sulfate-containing solutions. In batch electrolysis of 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solutions, at current densities of 13 to 28 mA/cm^2, coulombic efficiencies for urea oxidation of 18 to 54% were observed.

For 30 kg/m^3 urea solutions in the presence of the cell separator, the relative ratio of nitrogen to oxygen is plotted as a function of current density in Figure 7. Minimal nitrogen evolution was observed for the 100 mol/m^3 Na_2SO_4 + 30 kg/m^3 urea solution. The N_2/O_2 ratio increased to very large values as the chloride concentration increased from 0 to 10 to 100 mol/m^3 and as the current density was increased.

Kinetics of gas evolution and urea consumption

Figure 8 shows the course of oxygen and nitrogen evolution from the electrolysis of a 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solution in the absence of a cell separator. Figure 9 presents data on urea concentration as a function of charge passed for the experiment of Figure 8 and another identical experiment. In these experiments the coulombic efficiencies for urea oxidation and water electrolysis were 36 and 64%, respectively. The linear decline in urea concentration in Figure 9 reflects a constant rate of urea oxidation, even though the urea concentration decreased by a factor of five.

While the Nafion separator had no effect on polarization curves, the presence of the cell separator induced a substantial decrease in the nitrogen evolved during the electrolysis of pH 7.5 phosphate-buffered 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solution, as shown in Figure 10. The presence of the separator caused the anolyte pH to drop below 2, but in the cell without the separator, pH values never dropped below 6.8. If the anolyte was strongly buffered to pH 9.9, substantial nitrogen evolution was observed from the cell with the separator, as also shown in Figure 10.

Nitrogen evolution profiles from the electrolysis of 2,000 mol/m^3 NaCl + 0.50 kg/m^3 urea and 2,000 mol/m^3 NaCl + 30 kg/m^3 urea solutions in the presence of the cell separator were similar to the profile shown in Figure 10 for electrolysis of pH 7.5 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solutions in the presence of the cell separator. These low rates of nitrogen evolution were observed even though the coulombic efficiency for oxygen evolution was only 5% in the 2,000 mol/m^3 NaCl solutions.

In contrast to the behavior for the 0.50 kg/m^3 urea solutions, substantial nitrogen evaluation was observed during the electrolysis of 100 mol/m^3 NaCl + 30 kg/m^3 urea solutions in the presence of the cell separator, Figure 11. Only minimal nitrogen evolution was observed for 100 mol/m^3 Na_2SO_4 + 30 kg/m^3 urea solutions.

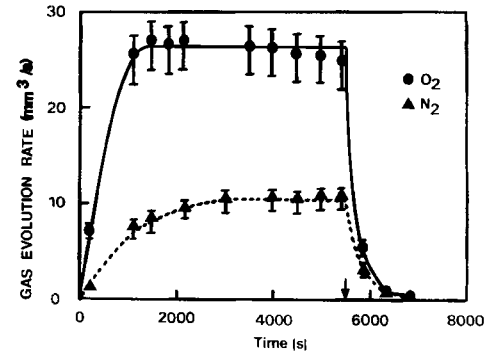


Figure 8. Oxygen and nitrogen evolution during electrolysis of pH 7.5 phosphate-buffered 100 mol/m^3 NaCl + 0.50 kg/m^3 urea in the absence of a cell separator.

Arrow indicates end of electrolysis; i = 28 mA/cm^2.

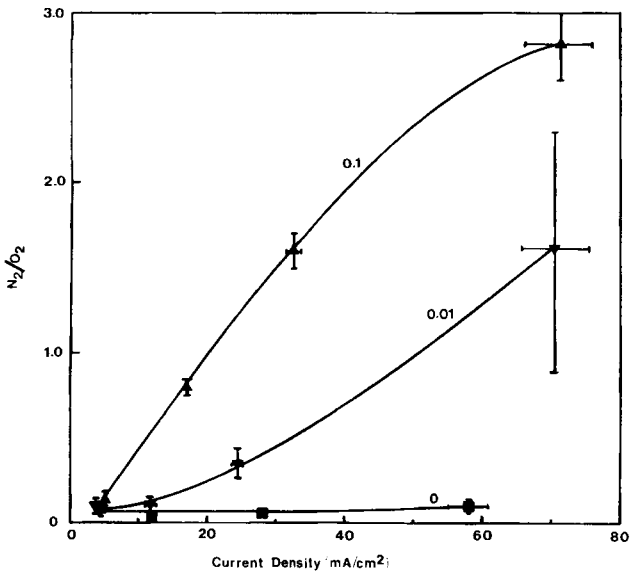


Figure 7. Nitrogen/oxygen ratio in product gas from electrolysis of pH 7 phosphate-buffered solutions containing 30 kg/m^3 urea.

■ 100 mol/m^3 Na_2SO_4 + 30 kg/m^3 urea; ▼ 10 mol/m^3 NaCl + 100 mol/m^3 Na_2SO_4 + 30 kg/m^3 urea; ▲ 100 mol/m^3 NaCl + 30 kg/m^3 urea.

All experiments were run in the presence of the Nafion separator.

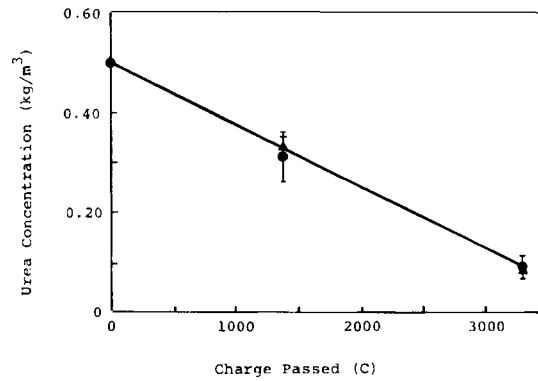


Figure 9. Urea concentration as a function of charge passed during electrolysis of pH 7.5 phosphate-buffered 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solutions in the absence of a cell separator.

i = 28 mA/cm^2

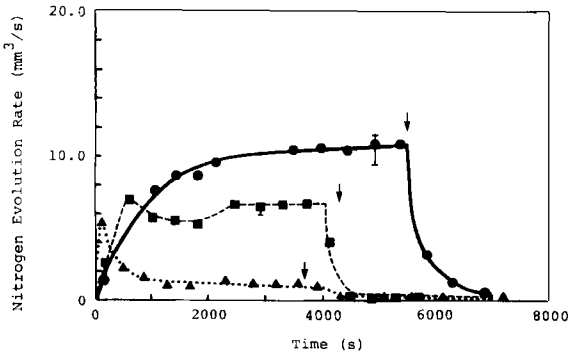


Figure 10. Nitrogen evolution from galvanostatic electrolysis of 100 mol/m³ NaCl + 0.50 kg/m³ urea.

i = 28 mA/cm²; arrows indicate end of electrolysis.
● pH 7.5 buffered in cell without separator; ▲ pH 7.5 buffered in cell with Nafion separator; ■ pH 9.9 buffered in cell with Nafion separator.

Table 1. Compounds Observed During Electrolysis of Urea + NaCl Solutions in the Presence of Nafion Separator

Urea kg/m³	NaCl mol/m³	Current Density mA/cm²	Compound(s)*
0.50	100	4	D + M
0.50	100	14	D + M
0.50	100	28	D
0.50	100	61	D
2.0	100	4	M
2.0	100	16	M
2.0	100	20	M
2.0	100	26	D + M
2.0	100	28	M
2.0	100	55	D
0.50	2,000	14	D
30.0	2,000	14	M
30.0	100	28	—

*D, dichlorourea; M, monochlorourea.

Chlorinated intermediates

In the electrolysis of pH 7.5 phosphate-buffered 100 mol/m³ NaCl + 0.50 kg/m³ urea solutions in the absence of the Nafion separator, residual chlorine levels (due to O—Cl or N—Cl species) of 0.7 mol/m³ were observed. What was presumed to be dichlorourea was the major species observed in UV spectra taken during electrolysis, but monochlorourea was observed after electrolysis. With the separator installed in the cell and with the anolyte initially at pH 7.5, residual chlorine levels of 10 mol/m³ were observed in the electrolysis experiments, but when the anolyte was initially buffered at pH 9.9, residual chlorine levels were 2 mol/m³.

The intermediate products observed during electrolysis of NaCl solutions containing urea are dependent on current density, as shown in Table 1. For the 100 mol/m³ NaCl solutions, at lower current densities monochlorourea or a mixture of monochlorourea and dichlorourea was observed, whereas at higher current densities dichlorourea was observed. For the 100 mol/m³ NaCl solutions, increasing the urea concentration increased the current density necessary for observation of dichlorourea.

For the 2,000 mol/m³ NaCl solutions, increasing the urea concentration from 0.50 kg/m³ to 30.0 kg/m³ resulted in monochlorourea being observed instead of dichlorourea. For the 100 mol/m³ NaCl + 30 kg/m³ urea solutions, neither monochlorourea nor dichlorourea was observed.

Chemical oxidation experiments

Figure 12 presents data on nitrogen evolution rate as a function of time for the chemical oxidation experiments. Nitrogen was a reaction product, just as in the case of urea electrooxidation. Further, the rate of nitrogen evolution increased with pH. From Reactions 2 and 3, if active chlorine is injected into a urea solution, one mole of nitrogen should be generated for each mole of consumed urea. At pH 4.5 and pH 7.5, the values of most interest for comparison with the electrooxidation experiments, the consumed urea equaled the evolved nitrogen to within ±10%. From Reactions 2 and 3, three moles of active chlorine

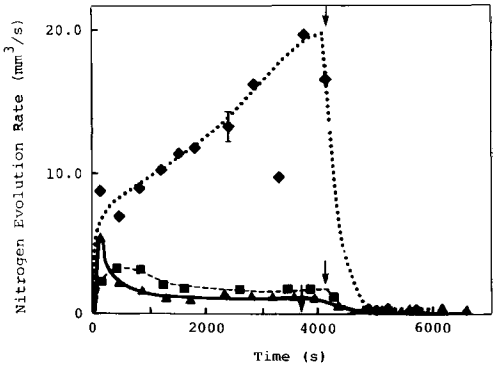


Figure 11. Nitrogen evolution from electrolysis of urea-containing pH 7 phosphate-buffered solutions in the presence of the Nafion separator.

▲ 100 mol/m³ NaCl + 0.50 kg/m³ urea; ♦ 100 mol/m³ NaCl + 30 kg/m³ urea; ■ 100 mol/m³ Na_2SO_4 + 30 kg/m³ urea.
i = 28 mA/cm² for all experiments; arrows indicate end of electrolysis.

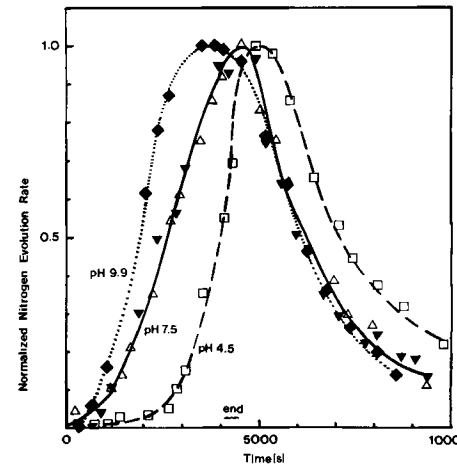


Figure 12. Nitrogen evolution from the chemical oxidation of 100 mol/m³ NaCl + 0.5 kg/m³ urea solutions by active chlorine.

Nitrogen evolution rate normalized with respect to maximum nitrogen evolution rate; "end" indicates termination of active chlorine addition.

should be consumed for every mole of oxidized urea. At pH 4.5 and pH 7.5 the ratio of active chlorine added to consumed urea was 3:1 within ±10%.

UV spectra taken during the chemical oxidation experiments revealed the presence of monochlorourea and what is presumed to be dichlorourea. Residual chlorine levels (due to O—Cl or N—Cl species) were on the order of 5 mol/m^3.

Discussion

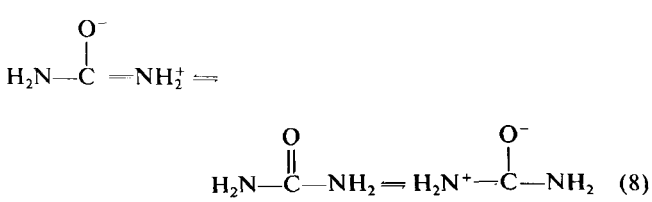
Electrooxidation reaction products

For the urea + NaCl solutions representative of spent dialysate (i.e., 100 mol/m^3 NaCl + 0.50 kg/m^3 urea), the major gaseous products from electrolysis in the absence of a cell separator are nitrogen (from urea oxidation), oxygen (from water oxidation), and hydrogen (from the cathodic reduction of water). Coulombic balance was observed, thus indicating that all major electrolysis products had been identified. Urea consumption balanced nitrogen evolution. Since molecular nitrogen is the product of urea nitrogen, carbon dioxide should be the product of urea carbon, as postulated in Reaction 3 or 4. This assumption is supported by the observation of CO_2 in the gaseous phase, as well as by certain observed pH changes attributed to CO_2 generation (see Wright, 1982, for details). Therefore, the overall reaction is as written in Reaction 5.

At low anolyte pH (as occurs in the presence of a cell separator), Reaction 5 does not proceed to completion, with high concentrations of chlorinated intermediates (monochlorourea and dichlorourea) being observed.

Urea adsorption

Urea depressed the observed current densities for both NaCl and Na_2SO_4 solutions (Figures 2, 3, 4). This behavior indicates that urea adsorbs on the RTTOE and blocks reaction sites, a conclusion that was confirmed by cyclic voltammetric experiments reported elsewhere (Wright, 1982). Urea adsorption appears characteristic of noble metal electrodes, also having been reported for the platinum electrode (Gromyko et al., 1979; Horanyi et al., 1979). Urea is thought to have a dipole-type resonance stabilized structure, as shown below (Sidgwick, 1966; Horanyi et al., 1979), which enhances its adsorption on electrode surfaces:



The Tafel slopes for urea-free 100 mol/m^3 NaCl (Figure 2) and urea-free 100 mol/m^3 Na_2SO_4 (Figure 3), and for 100 mol/m^3 NaCl + 0.50 kg/m^3 urea (Figure 2), were equal within experimental error, thus implying that the major electrodic event reflected in these polarization curves is the electrolysis of water. This conclusion is consistent with the N_2/O_2 data of Figure 6 and the coulombic efficiencies of 18 to 54% for urea oxidation. The addition of 0.50 kg/m^3 urea to 100 mol/m^3 Na_2SO_4 increases the Tafel slope to 180 mV/decade. Given the low rate of urea reaction in 100 mol/m^3 Na_2SO_4 (Figure 6), the increase in Tafel slope must be due to urea adsorption. In 100 mol/m^3 NaCl, 0.50 kg/m^3 urea did not alter the Tafel slope, and higher urea concentrations resulted in greater decreases in current density. Therefore, for 100 mol/m^3 NaCl solutions the RTTOE surface is not at saturation urea coverage when the bulk solution urea concentration is 0.50 kg/m^3.

Electrooxidation mechanism for solutions representative of spent dialysate

Three possible mechanisms must be considered for solutions representative of spent dialysate (100 mol/m^3 NaCl + 0.50 kg/m^3 urea):

1. Direct electrode reaction of urea.
2. Electrode reaction of adsorbed urea and a chloride or chlorine species.
3. Solution oxidation of urea by anodically generated active chlorine.

Urea adsorption would be consistent with direct electrode reaction. However, from the experiments of Figure 6 there is minimal nitrogen evolution (and low coulombic efficiencies for urea oxidation) in 100 mol/m^3 Na_2SO_4, as opposed to 100 mol/m^3 NaCl. The lower rate of reaction in 100 mol/m^3 Na_2SO_4 could be due to either lower electrode potential or the displacement of adsorbed urea from the RTTOE surface by adsorbed sulfate ions. From Figures 2 and 3, for the same current density, higher anode potentials are required in urea-containing 100 mol/m^3 Na_2SO_4 solutions, as compared to urea-containing 100 mol/m^3 NaCl solutions, and urea adsorbs on the RTTOE in the presence of sulfate ions.

A direct electrode reaction of adsorbed urea and an adsorbed chloride/chlorine species would be expected to affect the Tafel slope, but this is not observed in Figure 2 for the 0.50 kg/m^3 urea solutions. For the experiments of Figure 9, because of the simultaneous oxidation of water with a coulombic efficiency of 64%, the electrode potential remained essentially constant. Therefore, the urea oxidation rate was constant at constant potential even though the urea concentration decreased by a factor of five. If the oxidation mechanism involves direct electrode reaction of adsorbed urea and a chloride/chlorine species, then the reaction order (with respect to bulk solution urea concentration) must be zero. Zero reaction orders are usually associated with surfaces saturated with reactant; however, as discussed above, the RTTOE surface is not saturated with adsorbed urea in 100 mol/m^3 NaCl solutions. Further, the products of a zero-order electrode reaction should not change with current density. The results given in Table 1 show that the intermediate reaction product changed from monochlorourea to dichlorourea as the current density increased.

The solution oxidation mechanism is consistent with the lack of effect of 0.50 kg/m^3 urea on the Tafel slope in 100 mol/m^3 NaCl, and the mechanism is consistent with the increase with current density of the N_2/O_2 ratio, as shown in Figure 6. For urea-free chloride solutions, the coulombic efficiency for chlorine evolution increases with current density; this reflects the different Tafel slopes for O_2 and Cl_2 evolution (Hine et al., 1979).

The chemical oxidation experiments revealed no significant differences between electrooxidation and chemical oxidation. For both processes, with the pH maintained close to 7, the evolved nitrogen equaled the consumed urea. The presence of

the electrochemical cell separator caused the pH to drop and markedly reduced nitrogen evolution. For chemical oxidation, the rate of nitrogen evolution decreased with decreasing pH. For both processes, the same chlorinated intermediates were observed (monochlorourea and dichlorourea).

It can therefore be concluded that for 100 mol/m^3 NaCl solutions containing up to 0.50 to 1.0 kg/m^3 urea (i.e., for solutions encountered in dialysate regeneration), the electrooxidation mechanism is solution oxidation by anodically generated active chlorine. The major steps in this mechanism are:

$$6Cl^- \rightarrow 3Cl_2(aq) + 6e^- \quad (9)$$

$$Cl_2(aq) + H_2NCONH_2 \rightarrow H_2NCONHCl + H^+ + Cl^- \quad (10)$$

$$Cl_2(aq) + H_2NCONHCl \rightarrow ClHNCONHCl + H^+ + Cl^- \quad (11)$$

$$Cl_2(aq) + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (12)$$

$$ClHNCONHCl + HOCl \rightarrow N_2 + CO_2 + 3Cl^- + 3H^+ \quad (13)$$

Active chlorine in Reactions 10 and 11 has been shown as $Cl_2(aq)$, since these reactions should occur in the anode diffusional boundary layer, which is acidic. If the current density is low ($i < 3$ mA/cm^2), then the flux of active chlorine out of the anode diffusional boundary layer will also be low, and monochlorourea is then the dominant intermediate compound observed. At higher current densities (approximately 20 mA/cm^2 or greater for 100 mol/m^3 NaCl + 0.50 kg/m^3 urea solutions), active chlorine will react with essentially all of the urea diffusing into the anode boundary layer via Reactions 10 and 11 to yield dichlorourea. Conversion of dichlorourea to nitrogen occurs via Reaction 13, which is a bulk solution process. In the absence of a cell separator, the bulk solution pH will be close to 7, so the active chlorine for Reaction 13 will be present as HOCl. The rate of Reaction 13 increases with pH.

Electrooxidation mechanism for higher chloride and urea concentrations

The solution oxidation mechanism would imply that for 2,000 mol/m^3 NaCl + 0.50 kg/m^3 urea solutions:

1. The Tafel slope should be close to that reported in the literature for concentrated chloride solutions, as is observed in Figure 4.

2. In the presence of the cell separator, minimal nitrogen evolution should occur, as was observed, and dichlorourea should be an intermediate product, as is reported in Table 1.

3. The coulombic efficiency for oxygen generation should decrease to low levels, due to the presence of 2,000 mol/m^3 NaCl, as is observed.

For 2,000 mol/m^3 NaCl + 30.0 kg/m^3 urea solutions, minimal nitrogen evolution and the production of monochlorourea would be expected, as is observed.

For 100 mol/m^3 NaCl + 30.0 kg/m^3 urea solutions, the mechanism would predict minimal nitrogen evolution and the observation of monochlorourea. This is not what occurs, but rather, there appears to be a direct electrode of urea that yields molecular nitrogen. This reaction must be electrochemical because the relative ratio of nitrogen to oxygen in Figure 7 increases with current density. The reaction appears to require:

1. High urea concentrations and relatively high ratios of urea to chloride; e.g., the reaction did not occur in 2,000 mol/m^3 NaCl + 30 kg/m^3 urea.

2. The presence of low amounts of NaCl; e.g., the reaction occurred in 30 kg/m^3 urea solutions containing 10 mol/m^3 and 100 mol/m^3 NaCl but not in the 30 kg/m^3 urea + 100 mol/m^3 Na_2SO_4 solution.

3. Electrode potentials in excess of 1,300 mV vs. SCE; the reaction was not observed at the lower potential employed in the electrolysis of 2,000 mol/m^3 NaCl + 30.0 kg/m^3 urea.

This reaction may be of importance for urine electrolysis applications.

Implications for dialysate regeneration system

For solutions representative of spent dialysate, the major products of urea solution electrolysis are the nontoxic compounds N_2, O_2, CO_2, and H_2. Intermediate chlorinated products are formed, and a cell zone of approximately pH 7 or greater appears necessary for the efficient conversion of these intermediate compounds via Reaction 13 above. Such a zone would be provided in a porous, flow-through electrode cell, with an anode-to-cathode flow geometry. Further research should address:

1. The optimal design of such a system to minimize the residual level of chlorinated intermediates.

2. The toxicity of these intermediates.

3. Additional methods (e.g., adsorption on activated carbon) to lower the residual level of chlorinated compounds below toxic limits, if necessary.

The electrodes in an electrochemical dialysate regeneration system must be reasonably stable. While ruthenium titanium oxide electrodes are stable in concentrated chloride solutions, they are reported to be of limited stability in dilute chloride solutions or solutions devoid of chloride (Hine et al., 1979; Yeo et al., 1981). In the present investigation, electrode lifetime appeared to be at least six months, but further investigation would be warranted.

The results of this study indicate that electrochemical dialysate regeneration via RTTOE may be feasible. Since the electrooxidation mechanism is solution oxidation by anodically generated active chlorine, urea removal could conceivably be accomplished by any chlorine-producing electrode.

Conclusions

1. In 100 mol/m^3 NaCl solutions, the products of urea (0.5 kg/m^3) electrooxidation at the RTTOE are N_2 and CO_2. O_2 is generated in significant amounts by the simultaneous oxidation of water. The cathode reaction product is H_2.

2. For solutions containing urea and chloride at concentrations representative of spent dialysate, the reaction mechanism is solution oxidation of urea by anodically generated active chlorine. At current densities on the order of 20 mA/cm^2 and above, urea is chlorinated in the anode boundary layer to monochlorourea and then dichlorourea. Dichlorourea reacts in a pH-dependent bulk solution reaction to yield N_2 and CO_2. This reaction mechanism also applies to urea solutions containing high concentrations of chloride (2,000 mol/m^3).

3. Efficient conversion of urea to N_2, CO_2, and H_2 via the above mechanism requires a reaction zone of approximately pH 7 or greater for rapid conversion of chlorinated intermediates such as dichlorourea. Provision for such a zone must be incorporated in the design of an electrochemical dialysate regeneration cell.

4. The results indicate that electrochemical dialysate regeneration via RTTOE may be feasible.

5. There exists a direct electrochemical reaction of urea that appears to require:

- High urea concentrations and relatively high ratios of urea to chloride
- The presence of low amounts of NaCl
- Electrode potentials in excess of 1,300 mV vs. SCE.

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Notation

i = current density, mA/cm^2
Q_{act} = actual charge passed
Q_{equiv} = equivalent charge
Q_{N_2} = equivalent charge for nitrogen evolution, 6F/mol N_2
Q_{O_2} = equivalent charge for oxygen evolution, 4F/mol O_2
$Q_{resid\ Cl}$ = equivalent charge for residual chlorine, 2F/mol residual chlorine

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