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ELECTROCHEMICAL REDUCTION OF CHLORINE ON CARBON IN MOLTEN LITHIUM CHLORIDE - POTASSIUM CHLORIDE

by Andrew E. Potter and Betty S. Del Duca

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

Chronocoulometry was used to study the reduction of chlorine on pyrolytic graphite in molten lithium chloride - potassium chloride from 410^o to 500^o C. The amount of chlorine adsorbed on pyrolytic graphite in the molten salt at 1 atmosphere chlorine pressure was found to be approximately 1×10^{-11} equivalents per square centimeter. The reduction of chlorine was diffusion-limited for overvoltages larger than 56 millivolts, and the average diffusion coefficient was 0.3×10^{-5} square centimeter per second, assuming a chlorine solubility of 1×10^{-5} moles per cubic centimeters.

Double-layer capacitances for the pyrolytic graphite ranged from 48 to 62 microfarads per square centimeter. Activated charcoal electrodes were also studied. The amount of chlorine adsorbed by the activated charcoal was found by coulometry to be about 3×10^{-5} equivalents per gram, or about 3×10^{-11} equivalents per square centimeter, similar to graphite.

INTRODUCTION

The chlorine-carbon electrode has been used as a cathode for molten salt electrochemical cells using lithium as the anode material (refs. 1 and 2). Such cells show very high energy and power densities, and may be useful for vehicle propulsion or similar applications. This study was undertaken to evaluate the performance of activated charcoal, porous graphite, and pyrolytic graphite as chlorine cathodes in a molten lithium chloride - potassium chloride (LiCl-KCl) eutectic mixture. The objectives were to determine the rate limiting process for chlorine reduction at moderate overvoltages, and to measure the amount of chlorine adsorbed on the carbon surfaces.

Potentiostatic pulses were used to study the reduction of chlorine on pyrolytic graphite electrodes. The amount of chlorine gas adsorbed on the electrode surface, the

capacitance of the electrode, and the diffusion coefficients of chlorine in the electrolyte were determined.

Galvanostatic pulses were used to study the porous graphite and the activated charcoal electrodes. For the activated charcoal electrode, the amount of adsorbed chlorine and the length of time the adsorbed chlorine could be retained by the electrode were determined.

THEORETICAL

Chronocoulometry is used to study the chlorine electrode in molten chlorides. Christie, Lauer, and Osteryoung (ref. 3) have reported a chronocoulometric technique suitable for the study of electrodes having adsorbed reactants. A potential step is applied to the electrode, and the resulting current is integrated to give the number of coulombs of charge which pass through the electrode as a function of time. It is assumed that the time required to remove adsorbed reactant and to charge the double layer is negligible, and that the current is diffusion-controlled. Under these conditions, the charge per unit electrode area Q which flows during the application of the potential pulse is the sum of three terms:

$$Q = \frac{2nF\sqrt{D_o}}{\sqrt{\pi}} *C_o \sqrt{t} + nF\Gamma_o + Q_{dl} \quad (1)$$

where

Q charge, C/cm^2

n number of electrons involved in reaction, equal to 2 for Cl_2

F Faraday, 96 500 C

D_o diffusion coefficient, cm^2/sec

$*C_o$ concentration of reactant, moles/ cm^3

t time, sec

Γ_o amount of adsorbed reactant, moles/ cm^2

Q_{dl} charge required to charge double layer, C/cm^2

This equation shows that a plot of Q against \sqrt{t} will have a slope of $2nF\sqrt{D_o} *C_o/\sqrt{\pi}$ and an intercept of $nF\Gamma_o + Q_{dl}$. Evidently, the amount of adsorbed

reactant Γ_o could be obtained from the intercept, if Q_{dl} were known. Christie, Osteryoung, and Anson (ref. 4) suggest that Q_{dl} and $nF\Gamma_o$ may be separated by measuring the charge passed when the potential is stepped back to its original value.

For the case where the product of the electrochemical reaction is not adsorbed and where electrochemical equilibrium is achieved rapidly, the charge-time relation after a potential step of duration τ is given by

$$Q_r = \frac{2nF\sqrt{D_o} *C_o}{\sqrt{\pi}} \left(1 + \frac{a_1 nF\Gamma_o}{Q_c} \right) \theta + a_o nF\Gamma_o + Q_{dl} \quad (2)$$

where

$$Q_r = Q_{(t=\tau)} - Q_{(t>\tau)}$$

$$Q_c = \text{total charge passed during forward process, } 2nF\sqrt{D_o} *C_o \sqrt{\tau}/\sqrt{\pi}$$

$$\theta = \text{reduced time equal to } \sqrt{t - \tau} + \sqrt{\tau} - \sqrt{t}$$

a_1, a_o slope and intercept of plot of $1 - (2/\pi)\sin^{-1}\sqrt{\tau/t}$ against $\theta/\sqrt{\tau}$. The values of a_1 and a_o depend only slightly on the values of $\theta/\sqrt{\tau}$ chosen

The straight line fitted to the $Q_r - \theta$ data will have a slope of

$$\frac{2nF\sqrt{D_o} *C_o}{\sqrt{\pi}} \left(1 + \frac{a_1 nF\Gamma_o}{Q_c} \right)$$

and an intercept of $a_o nF\Gamma_o + Q_{dl}$. Consequently, from the slopes and intercepts of the $Q_{(t<\tau)}$ against \sqrt{t} (eq. (1)) and Q_r against θ (eq. (2)) plots, it is possible to calculate both the amount of adsorbed reactant, and the charge on the double layer.

Should the product of the reaction not be completely and rapidly desorbed, if the reactant is slow to be adsorbed, or if the surface concentration of reactant does not immediately return to its initial value when the potential is stepped back, then equation (2) is not valid. Under these circumstances, exact determination of the amount of adsorbed reactant and the double-layer capacitance is not possible without developing a model and extending the theory for this case. Therefore, a less rigorous method must be used to evaluate the double-layer charging term in equation (1). One such method is to perform another chronocoulometric experiment using a potential step, but in the absence of reactant. The slope of a $Q - \sqrt{t}$ plot will be zero, and the intercept will be Q_{dl} . This value of Q_{dl} can be used with the intercept in the presence of reactant to get $nF\Gamma_o$.

The uncertainty in this method arises from the assumption that the double-layer capacitance is unchanged by the reactant.

As will be described in the next section, equation (2) did not apply to the chlorine electrode, and it was necessary to estimate Q_{dl} by performing a separate experiment in the absence of chlorine.

EXPERIMENTAL

Electrode System

The test electrode consisted of a thin pyrolytic graphite blade, shaped so that the cleavage planes of the graphite were exposed. The upper section of the electrode was sealed into Pyrex glass, exposing a test area of 0.7 square centimeter (0.3 by 1 by 0.05 cm) which could be positioned well into the body of the electrolyte. This electrode was cemented to a Pyrex support ring with a high-temperature ceramic cement. This cement was not allowed to come in contact with the melt, as it is slightly soluble. Zirconium ions introduced into the melt from this cement inhibited the graphite and thus prevented the chlorine electrode from reaching its normal potential.

Chlorine gas was bubbled continuously into the melt over the surface of the graphite working electrode. The gas bubbles had no effect on the data due to the short time scale of the experiment. The chlorine was obtained commercially with a stated purity of 99+ percent and was used without further purification. The pyrolytic graphite electrode responded rapidly to the introduction of chlorine, and steady potentials within 100 millivolts of those reported in reference 5 for the chlorine electrode were achieved within a few minutes. Porous graphite electrodes responded slowly and irreproducibly to chlorine, usually giving potentials several hundred millivolts less than the literature values of the chlorine electrode.

Four graphite rods were cemented symmetrically about the center test electrode and connected electrically to form a single counter electrode. This arrangement is shown in figure 1.

The reference electrode was made by placing a silver wire in a mixture of 0.1 molar silver chloride (AgCl) and LiCl-KCl. A glass capillary tube was sealed and blown out at the end to make a thin-walled vessel which was filled with the chloride mixture and silver wire. The reference electrode was cemented in place as shown in figure 1. This electrode is discussed in greater detail by Bockris, et al. (ref. 6). Some initial experiments were performed with a platinum wire reference electrode as described by Laitinen (ref. 7). The equilibrium potential of chlorine in these cells was observed to decrease steadily with time. Inspection of the test electrode revealed a pink-red deposit which chemical analysis showed to be primarily chlorides of platinum.

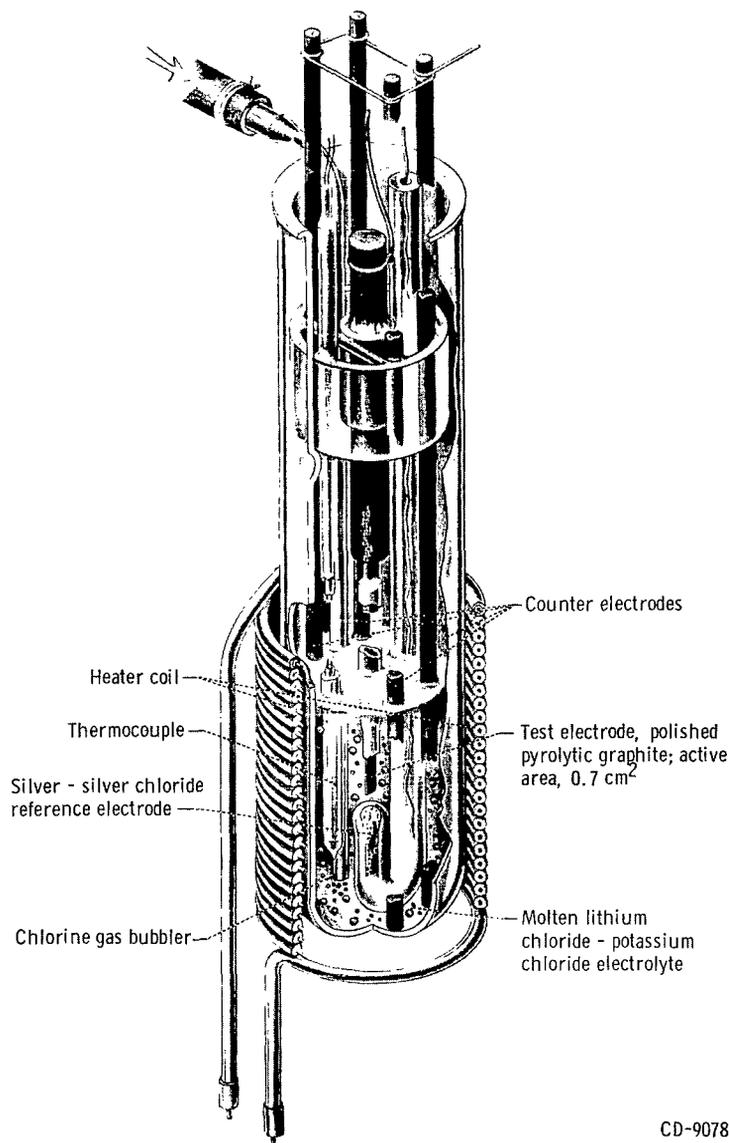


Figure 1. - Cell used in studies of chlorine electrode.

The cell container was made of Pyrex glass which appeared to have a longer life than quartz when used with hot LiCl-KCl. The temperature was controlled to $\pm 5^{\circ}$ C by a glass enclosed platinum - platinum rhodium thermocouple in the cell and a proportional controller. A resistance heating coil was wrapped around the outside of the cell and the assembly was covered with several layers of Pyrex wool to insulate the unit from air currents.

The purest commercially available materials were used throughout. The LiCl-KCl eutectic was commercially purified by vacuum distillation. The purity of the mixture was

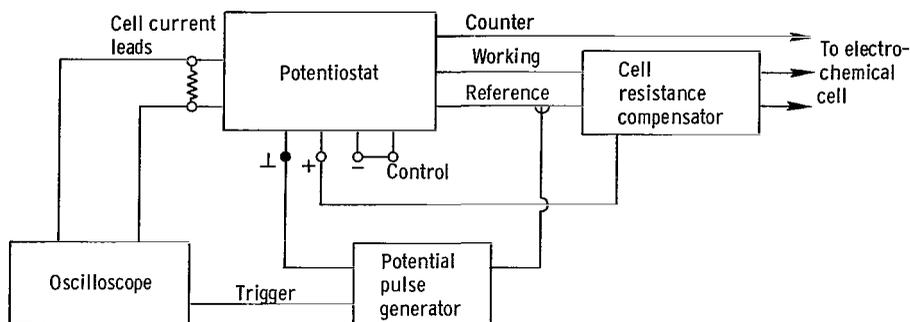


Figure 2. - Schematic diagram of electronic circuit.

such that it yielded a residual current of <2 microamperes at 2.2 volts and at 410° C with 1 square millimeter platinum electrodes. The pyrolytic graphite was a high-density graphite, and was formed in rods $1/8$ by 6 inches (0.31 by 15 cm) with the cleavage plane parallel to the axis of the rod. The activated charcoal was a standard commercial grade of activated coconut charcoal. The porous graphite electrodes were made from spectroscopically pure graphite rods. No pretreatment of the carbons was performed other than cutting and shaping.

A block diagram of the electronic measuring circuit is shown in figure 2. A fast-rise Wenking potentiostat was used to maintain the desired potential of the test electrode. A mercury relay-pulse generator of conventional design supplied a potential pulse of the selected length and magnitude to the control circuit of the potentiostat. The pulse was triggered by a Tektronix 535A oscilloscope. The resulting current trace was measured as a voltage across a standard resistance of 100 ohm, displayed on an oscilloscope, and photographed. To obtain the charge, the current traces were integrated directly from the photographs with a planimeter.

In addition to the main components pictured in figure 2, a circuit was added to correct for uncompensated resistance in the electrochemical cell. Uncompensated resistance is the electrical resistance of the electrolyte between the reference electrode and the surface of the working electrode. The presence of this resistance causes the potential at the working electrode to be less than the potential applied to the control circuit of the potentiostat by an amount proportional to the current through the cell. Significant errors in potential step experiments can result, since large currents flow initially during charging of the double layer. Essentially, the circuit designed by Lauer and Osteryoung (ref. 8) was used to accomplish the correction. The only difference involved the use of a small resistance to ground rather than a current follower, to obtain a control voltage correction proportional to current. The schematic of our circuit is shown in figure 3. Operational amplifiers used were differential operational amplifiers with a direct-current gain of 50 000 and a gain of unity at 2 megacycles. Exact compensation was achieved by increasing the feedback until oscillation of the current trace was observed

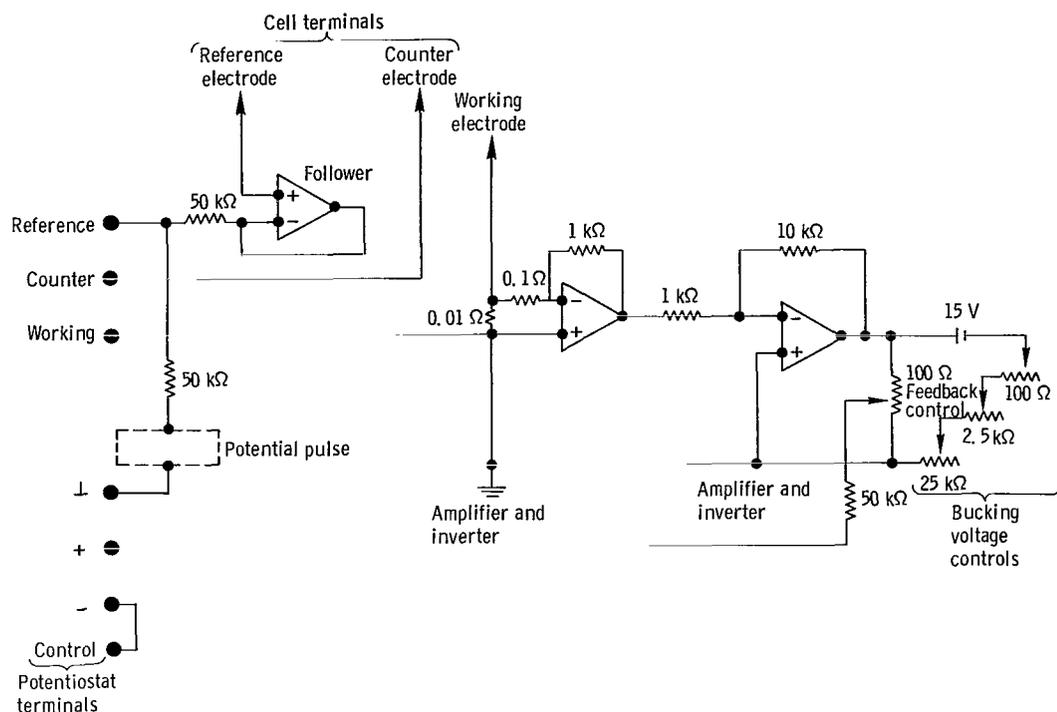


Figure 3. - Circuit used to correct for uncompensated resistances in cell.

(as described by Lauer and Osteryoung (ref. 8)). The circuit shown in figure 3 was not wholly satisfactory, in that it was difficult to obtain exactly equal amounts of feedback for cathodic and anodic pulses.

Test of Electrochemical System

Initial studies of the chlorine electrode produced plots of Q against \sqrt{t} which were not linear for times less than 0.4 millisecond. It was expected that the frequency response of the system should be better than this, so the potentiostatic pulse system was tested with a "dummy" electrode. The dummy electrode was a 25 microfarad condenser in parallel with a 1000 ohm resistor. The electrical properties of this circuit were similar to a typical graphite blade electrode immersed in the molten salt in the absence of chlorine. When potentiostatic steps were applied to the dummy electrode, traces very similar to those previously observed with the electrochemical cell were produced. A typical charge against time trace is shown in figure 4. Just as for the chlorine electrode, the plot does not become linear until about 0.4 millisecond. Attempts to overcome this poor response time were unsuccessful.

At 0.4 millisecond, the time at which the trace became linear, the charge passed Q

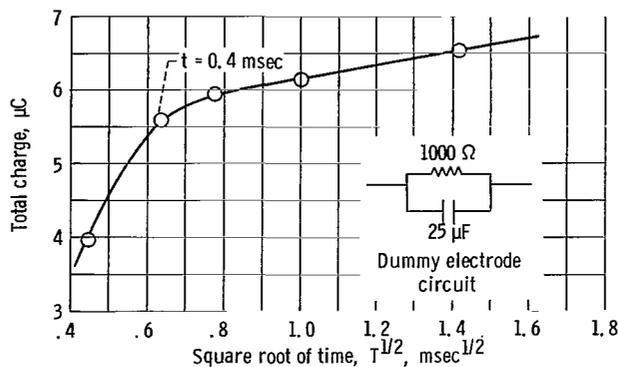


Figure 4. - Dummy electrode simulating an argon-filled cell. Potential pulse, 220 millivolt.

divided by the voltage pulse ΔV was 24.8 microfarads, in close agreement with the value of the condenser in the dummy electrode circuit. Capacitance was also estimated from the initial slope of current against time curves for the dummy electrode. This capacitance was independent of the size of the capacitor in the dummy electrode and was about 36 microfarads. This result lends support to the conclusion that the current during the initial 0.4-millisecond interval represented a limiting response of the instrument and was not usable for any measurement.

To determine the values of Q_{dl} and $nF\Gamma_0$ from Q against \sqrt{t} plots, it is necessary to extrapolate Q to zero time. Because of the long response time of the circuit, it is evident that extrapolation to the actual zero of time when the pulse is applied will yield intercepts that are too small. A better procedure is to extrapolate to a fictitious zero-time which is the time at which the double layer is nearly fully charged. This time is approximately 0.4 millisecond obtained with the dummy electrode. The slope of the charge against time curve is such that an uncertainty of about ± 0.1 millisecond is attached to this "zero" time.

In order that the chronocoulometric equations (1) and (2) shall apply, the current produced by the potential step must be diffusion controlled after charging of the double layer and removal of adsorbed reactant. To test this for the chlorine electrode, the current produced by a potential step was measured as a function of time. If the current is diffusion controlled, it will vary as the -0.5 power of time (refs. 3 and 4). The current-time behavior was measured for potential steps ranging from 100 to 800 millivolts over a wide time range. The current varied as the -0.5 ± 0.1 power of time, for times ranging from one to several thousand milliseconds. Thus it can be assumed to be diffusion controlled.

For a diffusion-controlled reaction, plots of charge against time, according to equations (1) and (2), should be linear for times greater than 0.4 millisecond, the fictitious zero time. A test is shown in figure 5, where data for the application of 2.7-millisecond, 170-millivolt cathodic pulse are shown. The charge passed when the potential step is ap-

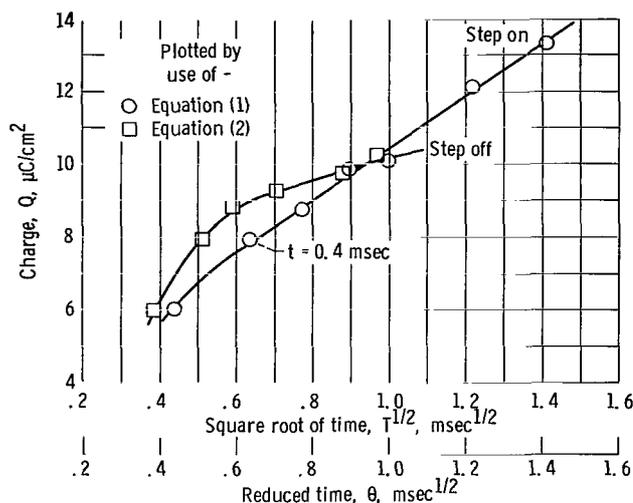


Figure 5. - Chlorine-filled cell. Temperature, 600° C; cathode pulse, 170 millivolts, 2.7 milliseconds.

plied ("step on") is plotted according to equation (1). The data fall on a straight line, indicating that equation (1) is valid for this experiment. The charge passed when the potential is stepped back to its initial value ("step off") is plotted according to equation (2). These data fall on a curved line. If a straight line is through the data for $\theta > 0.4$, the slope of this line is less than for the "step on" plot, and the intercept is higher. These results are inconsistent with equation (2), and evidently this equation does not apply to the chlorine electrode. A possible explanation for this may be that the graphite does not seem to reach equilibrium with the chlorine in the electrolyte very rapidly. As a result, when the potential is stepped back to the equilibrium value, excess chlorine is generated electrochemically. This is troublesome in this particular case because a high concentration of chloride ion is present at all times. This contrasts with the usual practice in which the concentration of oxidizable material is only that produced by the cathodic step and is completely consumed following the off step.

Since equation (2) could not be used to determine the double-layer charging correction, it was necessary to perform a separate experiment, using argon in place of chlorine. The steps had as their initial potential, the equilibrium potential of the electrode in argon, which was usually about 160 millivolts relative to the Ag - AgCl reference. It was found that the value of the initial potential had very little effect on Q_{dl} . Also, anodic and cathodic pulses gave identical results within experimental error. Anodic steps were generally used.

RESULTS

Chronocoulometric experiments in the presence and absence of chlorine allow deter-

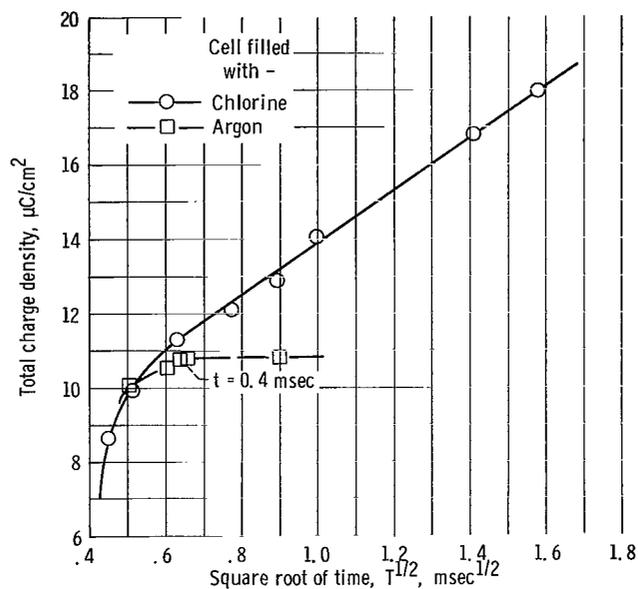


Figure 6. - Typical results of chlorine coverage determination for chlorine- and argon-filled cells. Cathodic pulse, 120 millivolts; test electrode, pyrolytic graphite.

mination of three experimental quantities from Q against \sqrt{t} plots: (1) the amount of chlorine adsorbed on the surface of the electrode, (2) the double-layer capacitance of the electrode, and (3) the diffusion coefficient of chlorine gas in the electrolyte.

The chronocoulometric experiments were performed over a temperature range of 410° to 500° C for applied cathodic potential steps of 108 to 800 millivolts.

Figure 6 shows a Q against \sqrt{t} plot typical of those obtained in the determination of chlorine coverage. The solid curve is a plot of total charge per unit electrode area against \sqrt{t} for a chlorine-filled cell. The dashed curve is that obtained for the argon-filled cell. When $t = 0.4$ millisecond is assumed to be the zero time as previously discussed, the difference in total charge at this time is taken as a measure of the number of coulombs used in cathodically removing adsorbed chlorine from the surface. The effective zero time is uncertain by about ± 0.1 millisecond, which introduces a corresponding

uncertainty into the measurement of adsorbed chlorine. The amount of adsorbed chlorine was measured at several temperatures using a 220-millivolt pulse. The results are shown in table I. Any trend of the amount of adsorbed chlorine with temperature is masked by the experimental scatter. The average value is 1×10^{-11} equivalents per square centimeter, which represents a surface coverage of less than 0.4 percent of a monolayer, assuming the surface area to be the apparent geometric area (0.7 cm^2).

TABLE I. - AMOUNT OF ADSORBED CHLORINE ON GRAPHITE

Temperature, $^{\circ}\text{C}$	Equivalents per cm^2
410	$1.0 \pm 0.3 \times 10^{-11}$
430	$.5 \pm 0.3$
460	1.4 ± 0.7
500	1.0 ± 0.4

The integral double-layer capacitance of the pyrolytic graphite electrode was calculated from the relation

$$C_{dl} = \frac{Q_{0.4 \text{ msec}}}{\Delta V}$$

where

$Q_{0.4 \text{ msec}}$ total charge per unit area observed at $t = 0.4$ millisecond in argon-filled cell

ΔV applied pulse, V

The capacitances obtained for a pyrolytic graphite electrode at 410° C for different potential steps are shown in table II(a). The increase in capacitance with increasing the potential step is probably due to the electronic circuitry, because little or no change of capacitance was observed for different initial potentials or for the direction of the step, whether anodic or cathodic.

TABLE II. - INTEGRAL CAPACITANCE OF PYROLYTIC GRAPHITE
IN FUSED LITHIUM CHLORIDE-POTASSIUM CHLORIDE

(a) Effect of potential step at 410° C

(b) Effect of temperature at 220-millivolt potential step

Potential step, mV	Integral capacitance, $Q_{dl}/\Delta V$, $\mu\text{F}/\text{cm}^2$	Temperature, $^{\circ}\text{C}$	Integral capacitance, $Q_{dl}/\Delta V$, $\mu\text{F}/\text{cm}^2$
56	48±10	410	54±11
109	48±10	430	56±11
220	49±10	460	45±9
242	60±12	490	41±8
510	62±12		

The temperature dependence of the integral capacitance was measured for a 220-millivolt pulse, and these results are shown in table II(b). The capacitance at 220 millivolts and 410° C differs in table II because the experiments were performed on different days. Slow changes in electrode performance with time were always observed. The values of capacitance reported in tables II and III are in general agreement with those reported for other solid electrodes in fused salts (ref. 9).

The diffusion coefficients of chlorine gas in molten LiCl-KCl eutectic may be calculated from the slopes of plots of the total charge against \sqrt{t} . From equation (1), the

TABLE III. - POTENTIAL STEP

DEPENDENCE OF DIFFUSION

COEFFICIENTS AT 430° C

Potential step, mV	Diffusion coefficient, D, cm ² /sec
109	0.38×10 ⁻⁵
170	.47
305	.60
520	.75
800	1.58

TABLE IV. - CORRECTED DIFFUSION COEFFICIENTS

AT VARIOUS TEMPERATURES

Temperature, °C	Diffusion coefficient, D, cm ² /sec
410	0.27×10 ⁻⁵
430	.30
460	.41
490	.27

slope is equal to $4F\sqrt{D_0} * C_0 / \sqrt{\pi}$. Assuming a solubility of 10^{-5} moles of Cl₂ per cubic centimeter (private communication with G. Harrington, Temple University, Philadelphia, Pa.), diffusion coefficients were calculated from data taken at 430° C for various cathodic potential steps. These data appear in table III. The values on the diffusion coefficient D increase with the magnitude of the applied potential step. A much larger dependence was noted in early experiments without the resistance compensating circuit. This suggests that the resistance in the circuit may not be fully compensated, although no improvement could be made with the existing circuit. The data were corrected for the potential dependence effect by extrapolating the D values at 430° C to zero applied potential. This percentage correction was then applied to D values at all temperatures. The diffusion coefficients corrected for the potential effect are listed in table IV as a function of temperature. The diffusion coefficient does not seem to vary with temperature within our experimental error. The average value is $0.31 \pm 0.06 \times 10^{-5}$ square centimeter per second.

ADSORPTION OF CHLORINE ON ACTIVATED CHARCOAL BY COULOMETRY

The amount of chlorine adsorbed on the cleavage plane of graphite in fused salt at 400° to 500° C appears to be extremely small, from the results of the potentiostatic pulse measurements mentioned previously. This is in general agreement with the results of Cascarini, Voogd, and Arvia (ref. 10) who studied the adsorption of gaseous chlorine on pure graphite at temperatures near room temperature and found principally physical adsorption, with an activation energy of 1.9 kilocalories per mole (7953 J/mole). At 400° to 500° C, the amount of physically adsorbed chlorine will be very small. However, Cascarini noted some evidence for compound formation in the graphite interlayers. This would correspond to chemisorption of chlorine at 400° to 500° C. With this possibility in

mind, the adsorption of chlorine on a carbon known to have a high surface activity was studied, that is, activated coconut charcoal. The amount of chlorine adsorbed by the charcoal and the rate of loss from the charcoal by desorption into the electrolyte was measured.

Experimental

An activated charcoal electrode was prepared as shown in figure 7. A glass cloth disk was used to hold 0.1 gram of powdered activated coconut charcoal in contact with a

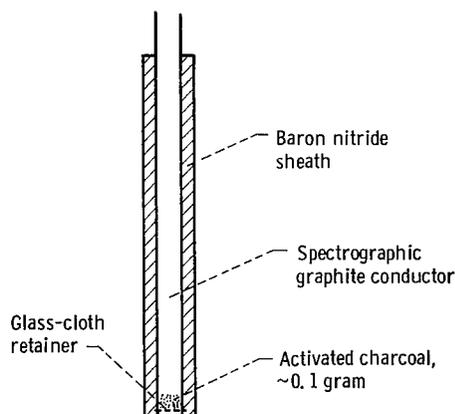


Figure 7. - Construction of activated charcoal electrode.

graphite rod. This electrode may be classed as a porous electrode. The potential step method is not very useful for the study of reactant adsorption on porous electrodes, because the resistance of the electrolyte in the narrow pores slows down the processes of double-layer charging and removal of adsorbed reactant. Our procedure for measuring chlorine adsorption was to saturate the electrode with electrochemically generated chlorine, then remove it stepwise by short cathodic current pulses. The potential of the electrode was measured after each pulse with an electrometer voltmeter. The total cathodic charge required to drive the electrode potential from the chlorine electrode potential to the equilibrium potential observed in an argon atmosphere was assumed to be equivalent to the total chlorine adsorbed on the electrode.

The current pulses were generated by a Wenking potentiostat operated as a galvanostat. The potential pulses applied to the galvanostat to produce the current pulses were produced by a mercury relay-battery combination triggered by the oscilloscope gate voltage.

It was observed that the electrode potential spontaneously decreased with time after the electrode had been electrochemically saturated with chlorine. Evidently, chlorine

desorbed and diffused into the electrolyte. It was necessary to measure the loss rate in order to know how rapidly to perform the cathodic stripping experiments.

Rate of Loss of Chlorine

The rate of chlorine loss was observed for three electrode types at 410⁰ C. In addition to the activated charcoal electrode, a pyrolytic graphite blade and a porous spectrographic graphite blade were studied. These blades were about 0.5 centimeter wide, 0.1 centimeter thick, and extended about 2 centimeters into the melt. Argon was bubbled through the melt to maintain an inert atmosphere. This experiment was performed by applying an anodic current pulse of sufficient magnitude and duration to achieve a steady potential, approximately the chlorine electrode potential, and then measuring the decay of the voltage with time after cessation of the pulse. Oscillographic plots of the voltage decay for three electrodes are shown in figure 8. An inflection point in the volt-

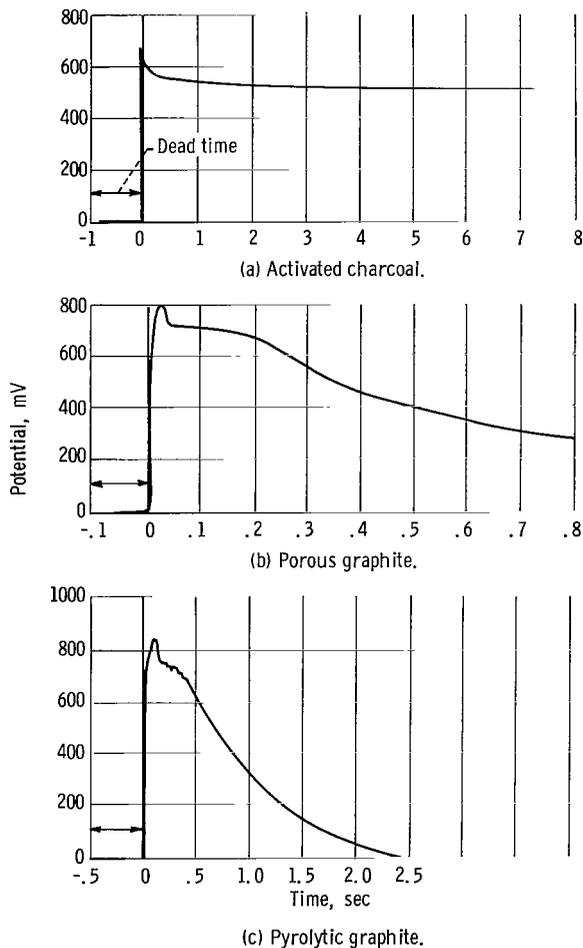


Figure 8. - Voltage decay for various carbon electrodes.

age against time plots occurs for the pyrolytic and porous graphite. A similar effect was reported by Murgulescu, Sternberg, and Medintev (ref. 11) for graphite-chlorine electrodes in molten AgCl. The origin of this inflection point is obscure, although they attributed it to desorption of strongly adsorbed chlorine. The activated charcoal electrode retained chlorine sufficiently well so that no potential loss could be observed in the time scale available to the oscilloscope. The potential decay for this electrode was measured with an electrometer voltmeter and a stop watch, with the results shown in figure 9. It is convenient to compare these three electrodes by defining a retention time, which is the time required for the potential to drop to half its initial value. Table V contains a summary of the retention time results.

The difference between the various carbons is considerable. It is evident that none of them store chlorine in a semipermanent fashion as might be expected if strong chemisorption occurred. Also, the time available for the cathodic stripping of chlorine from the activated charcoal electrode is short, with the potential dropping spontaneously by 0.1 volt in the first minute. However, after the potential drops below 0.6 volt, it decays much more slowly, at a rate of 0.005 volt per minute.

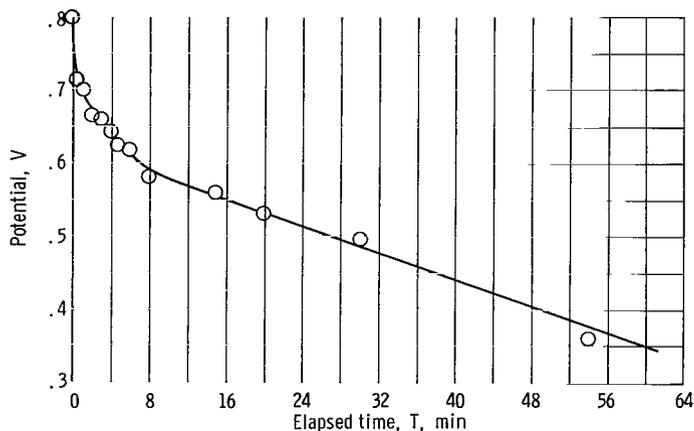


Figure 9. - Potential decay of activated charcoal electrode.

TABLE V. - RETENTION TIME OF CHLORINE
ON CARBON ELECTRODES

Electrode material	Retention time, sec
Pyrolytic graphite	0.75
Porous graphite	5.3
Activated charcoal	2800

Amount of Chlorine Adsorbed on Activated Charcoal

The amount of chlorine which could be stored on activated charcoal at 410° C was determined in the same way. The cathodic stripping pulses were applied as rapidly as possible, so that the whole experiment took about 5 minutes. The results are shown in figure 10. The bulk of the chlorine was removed at potentials below 0.6 volt, so that spontaneous losses were small. The total amount of chlorine stored was 3.4 coulombs per

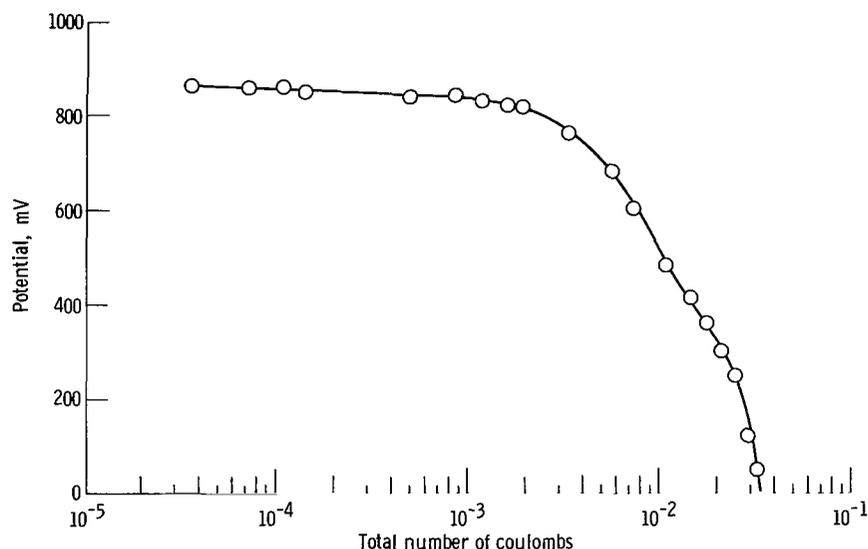


Figure 10. - Removal of chlorine from 0.1-gram activated charcoal by cathodic pulses.

gram of charcoal. Assuming a specific area of 100 square meters per gram of charcoal, this corresponds to about 3×10^{-11} equivalents per square centimeter. It should be noted that this number is of the same order of magnitude as that determined for the pyrolytic graphite electrode. The affinity of the two carbon surfaces for chlorine is apparently similar - the difference observed arising in the greatly increased surface area of the activated charcoal electrode.

CONCLUSIONS

Studies of pyrolytic graphite and activated charcoal show on the order of 1×10^{-11} equivalents of chlorine adsorbed per square centimeter at 400° to 500° C. The average diffusion coefficient of chlorine gas in molten lithium chloride - potassium chloride was found to be $0.31 \pm 0.006 \times 10^{-5}$ centimeter per second. The double-layer capacitance of the pyrolytic graphite electrode ranged from 40 to 60 microfarads per square centimeter.

None of the carbons studied proved useful for permanent storage of chlorine due to the high loss rate of chlorine to the electrolyte at temperatures between 400^o to 530^o C.

Lewis Research Center,
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