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A novel electrochemical process for the production of ammonium perchlorate

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Perchloric acid, $HClO_4$, and ammonium perchlorate, NH_4ClO_4, of high purity have been produced by electrolysis of chloric acid and subsequent reaction with high purity ammonium hydroxide to produce ammonium perchlorate. The process involves no alkali metals, chlorides or transition metals such as chromates, and thus produces propellant and explosive grade ammonium perchlorate of high purity and with no associated instability or pollution problems. The products can be recovered by solution crystallization-drying or direct spray-drying, respectively.

1. Introduction

The overall process developed by Olin starts with chlorine and caustic soda and forms hypochlorous acid chemically, as shown in the product tree in Fig 1. Chlorine reacts with caustic in a vapour phase process to produce hypochlorous acid, and this in turn is electrolysed to chloric acid, which is the starting material for the presently described process to produce perchloric acid and ammonium perchlorate. The present paper discusses the second electrolytic step in Fig. 1., that of electrolysis of chloric to perchloric acid [1]. In chloric acid the plus five oxidation state of the chlorine species is increased to plus seven through a unique anodic oxidation step in a cathode-membrane sandwich cell. This paper describes the oxidation of chloric to perchloric acid in the electrolytic cell, then the post reaction of perchloric acid to ammonium perchlorate in a spray drying system.

The preparation of perchloric acid is important because it is used in analytical chemistry to separate potassium from sodium, and also its salts are used for explosives, electromachining and in plating. One of its salts, ammonium perchlorate (AP) is used in explosives, pyrotechnic compositions, jet and rocket compositions. This is the product of great interest in the perchlorate family today for military and civilian rockets.

The objective of this project has been to develop a process to produce ultra-high purity perchloric acid from HOCl, and to verify the process viability to support the product innovation concept for producing perchloric acid and ammonium perchlorate with electrolytic oxidation progressing through the chlorine oxo acids $HOCl > HClO_3 > HClO_4$. This process avoids the use of calcium, magnesium, sodium, chloride and dichromate ions which conventionally must be used in the 2.5 to $5\,g\,dm^{-3}$ ranges to prevent cathodic reduction of ClO_3^- and ClO_4^- in conventional cells.

Small scale laboratory studies have been carried out to determine the feasibility for producing perchloric acid from J3® hypochlorous acid using a specially designed membrane cell. In the first step electrolytic oxidation is carried out to convert the HOCl into $HClO_3$; in the second step the electrolytic oxidation of $HClO_3$ to $HClO_4$, with this followed by ammoniation, crystallization, drying and finally, classification.

Extremely high purity ammonium perchlorate (AP) can be produced using this novel process of direct electrochemical oxidation of hypochlorous acid to chloric and finally perchloric acid, followed by ammoniation and spray-drying [1].

The most outstanding property of AP is its high oxygen concentration (54.5% O_2) and the fact that it decomposes without leaving a solid residue. Because of its strong oxidizing power and chemical stability, AP provides a reliable means of high energy oxidation under controlled conditions. It is especially useful when employed in a composite propellant with plastic fuel binder. In this application it dominates the field as the oxidizer of choice in high performance solid propellants. AP crystals thus constitute 70% of the ingredients of the solid fuel in rockets today.

The key requirements for solid propellants are burn rate, product purity, stability, and in addition, particle size distribution, which affects the burn rate. The presence of impurities impacts crystal growth, product stability, and overall process economics. The issue of product purity is so important that present conventional processes are operated at low efficiency in order to produce highly pure product, due to the extensive purification steps currently involved. Even though the solubility of AP is much less than sodium perchlorate, the presence of sodium leaves a residual 15 to 400 p.p.m. of sodium in the finished product under best conditions with current commercial technology.

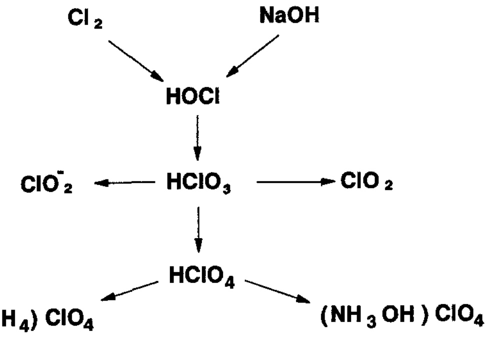

Fig. 1. Advanced oxidants from hypochlorous acid, product opportunities tree.

Current technology utilizes the electrochemical generation of hypochlorite followed by the disproportionation to chlorate and chloride as shown:

$$NaClO_3 + NH_4Cl + H_2O \Longrightarrow NH_4ClO_4 + NaCl + H_2 \qquad (1)$$

Dichromates are added in the electrolysis step to improve efficiency, adding to the impurities of salt and metals in the product.

Whereas, the Olin process starts with $HClO_3$ and involves no salt or dichromate. This new, Olin approach is depicted as

$$HClO_3 + H_2O \Longrightarrow HClO_4 + H_2 \qquad (2)$$

$$HClO_4 + NH_3 \Longrightarrow NH_4ClO_4 \qquad (3)$$

2. Experimental details

Electrode polarization studies were made using a standard current interrupt technique with a small 1.2 A, 12 V Hewlett Packard power supply, model 6214B, and a Keithley 614 electrometer and a model 3091 Nicolet storage oscilloscope. The current interrupt switch, which quickly turns off the current passing through the electrolytic cell so that *IR*-free electrode potentials can be measured, was built at Case Western Reserve University, in Cleveland, Ohio. A simple 'H' cell was used as shown in Fig. 2, with a 4 cm^2 cathode, DuPont 417 membrane, standard calomel reference electrode and 1 cm^2 working anode.

Electorchemical synthesis studies were conducted in a large cell shown in Fig. 3. It is comprised of two one litre glass vessels which are jacketed for temperature control, and connected through two inch glass pipe connectors. Each vessel is stirred with a magnetic stirrer. One unique feature of this electrolytic system is that the anode must be spaced from the membrane by a finite gap, about 0.1 inch, but in order for the cell to operate, the cathode must be put into intimate contact with the cathode side of the membrane, as shown in Fig. 4, which allows proton tunneling to occur through the membrane from the anode to the cathode facilitating continuous, low-voltage operations. The bench-scale reactor for electrolysis was

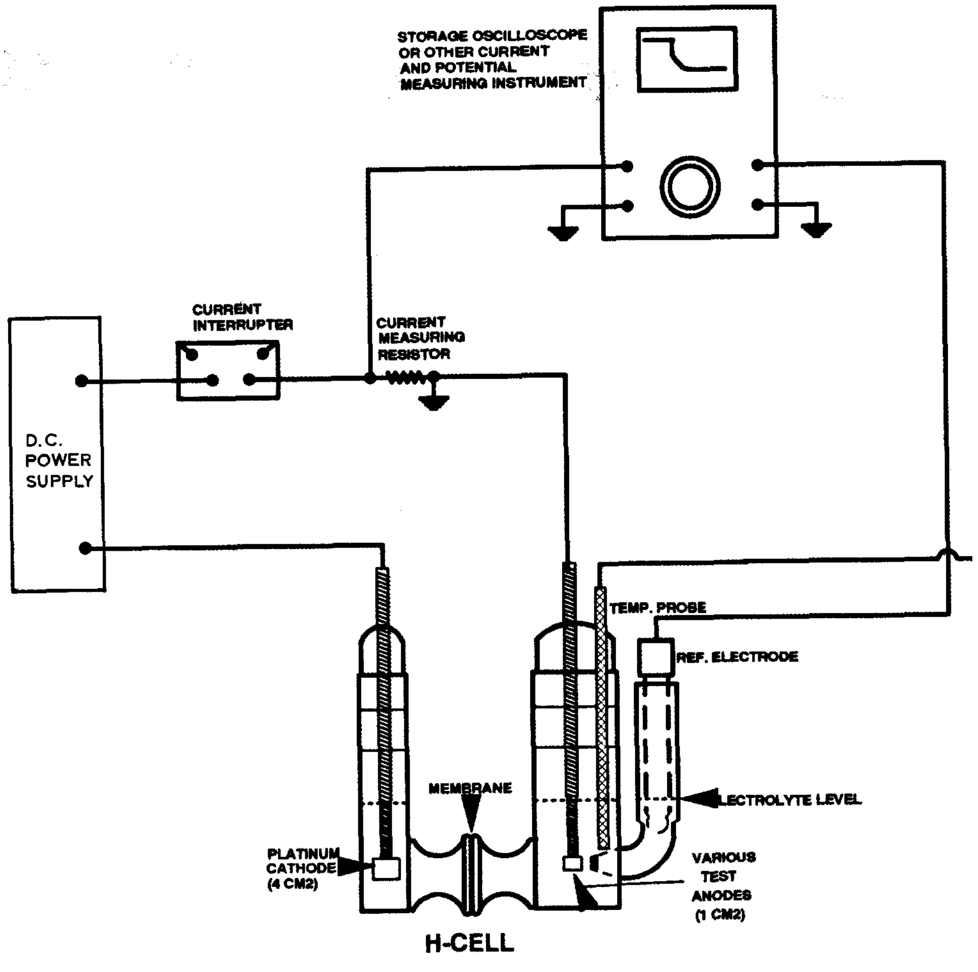

Fig. 2. Current interruption test apparatus.

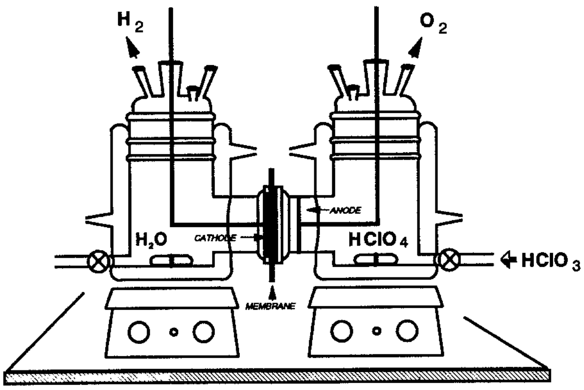

Fig. 3. Perchloric acid cell assembly.

manufactured by Hammett Scientific Glass, Belvedere, South Carolina.

The laboratory spray drying and granulating system used was a Pulvis Mini Spray/Mini Bed, Model GA-32/32 built by Yamato USA, in Northbrook, Illinois, is shown in Fig. 5. The GA-32 sprays solution in minute droplets which are instantaneously heated without exposure to excessively high temperatures, thus samples susceptible to extreme heat, such as ammonium perchlorate, are not damaged by this drying operation.

Figure 6 gives an overall process flow sheet for the operation, starting with chloric acid, water and electric power, adding ammonia to the crystal reactor and ending with the dry product.

2.1. *Anode polarization method*

Interruption of the current is frequently used to assess the magnitude of the ohmic drop which is included in the measurement of electrode potentials during the passage of current in a cell. This value so measured corresponds to the primary current distribution in the electrode system under study. The current interrupt technique is the simplest transient procedure, since it interrupts the current after a steady operating condition has been developed at the interface. This may occur before the concentrations have changed appreciably from their initial values just after opening the circuit, in which case convection is important. Interruption of current eleminates ohmic potential drop from the measurement, while the surface overpotential is maintained momentarily by the charge in the double-layer capacitor. When the current is interrupted, the double-layer capacity is left charged at the prevailing local value, and may then be discharged by means of a faradaic reaction, thereby yielding the true *ir* component of the dynamic electrode potential.

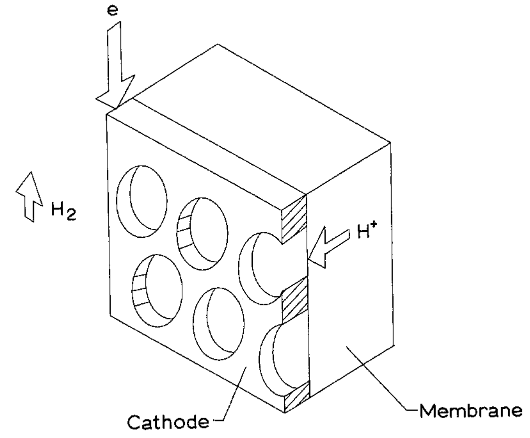

Fig. 4. Section of cathode-membrane sandwich showing proton transport through membrane and discharge on cathode.

The laboratory equipment for conducting the experiments on perchloric acid and ammonium perchlorate synthesis is shown in the Figures. Figure 2 shows the H Cell, interrupter switch, d.c. power supply and oscilloscope used for the current interrupter testing of various anodes for the cell. The current interrupt technique is needed to provide absolute values of the overvoltage measurements on various anodes [2]. The potential difference between working and reference electrode is

$$E_{W-R} = E_W - IR_U - E_R \qquad (3)$$

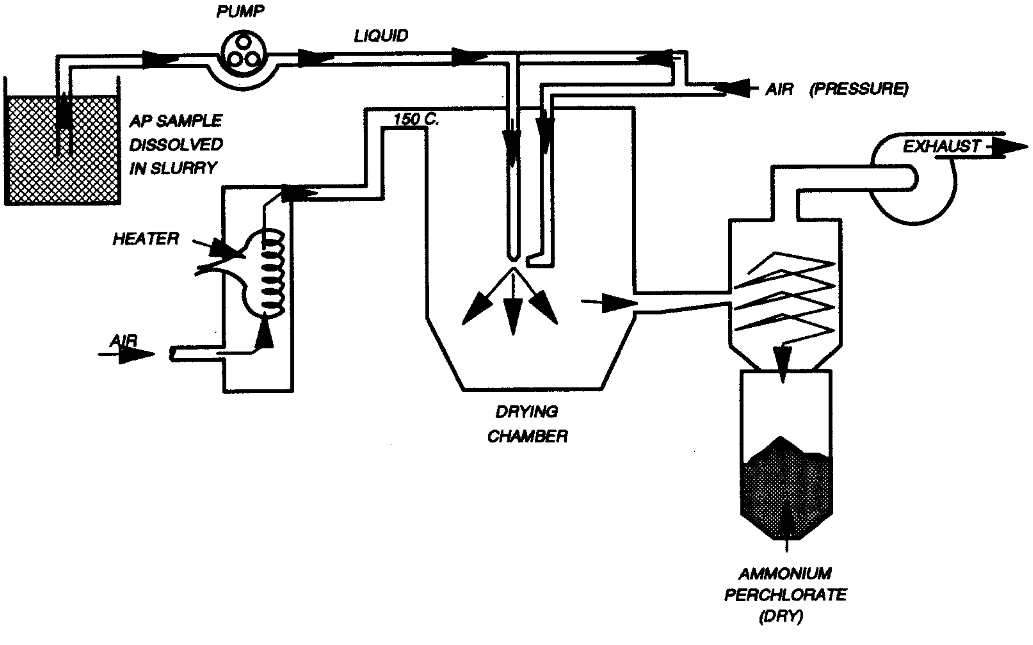

Fig. 5. Ammonium perchlorate spray drying system.

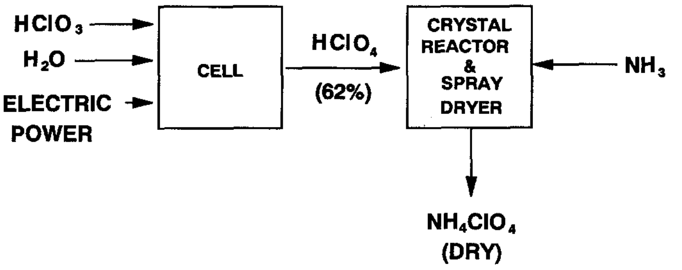

Fig. 6. Process flow sheet for chloric to perchloric acid and ammonium perchlorate.

where E_W and E_R are potentials which can be referred to ground at the working and Luggin probe, respectively. The system shown in Fig. 2 includes a fast trigger oscilloscope, current interrupter switch and power supply for the electrode studies [2, 3].

The simple interrupter technique described here permits the uncompensated resistance, R_U, in an electrochemical cell to be measured while the test electrode is under potentiostatic control. The ohmic potential drop, IR_U, can be monitored continuously as a function of the cell current, I, and the d.c. bias potential, and/or time. Very brief current interruption times must be employed if perturbation of fast electrode reactions is to be avoided. With fast-rise potentiostats, amplifier ringing persists for 1 μs or less. Interruption times of 5–10 μs are then of sufficient length to permit the ohmic potential drop to be determined. The shorter the interruption time, the more rapid is the recovery of the potentiostat. Perturbation times associated with the voltage and current pulse methods are in general considerably longer. Interrupter measurements can only be made when there is an appreciable direct current flowing through the cell. This procedure should also be useful for potentiostats having relatively slow response times.

2.2. Electrochemical polarization measurements

Figure 7 shows a plot of the anodic overvoltage over different ranges for a platinum anode in different concentrations of chloric acid at 25, 37 and 50 °C. This data was used to estimate the anode potentials required to produce perchloric acid efficiently.

It is observed that below 1 kA m^{-2} the overpotential is due to normal oxygen evolution for water electrolysis going through nascent oxygen, followed by oxygen exchange between chlorate to perchlorate. At high concentrations of chlorate or perchlorate, we see polarization curves produced by normal oxygen evolution, where high enough concentrations of oxo-anions provide the proper high conductivity low voltage kinetic path for coupling and disproportionation, as demonstrated by Knibbs and Palfreeman [4]. At the low concentrations of these ions the anode potential is high and nascent oxygen could be generated which oxidizes the chlorate to perchlorate, according to the mechanism of Bennett and Mack [5] due to the oxide film transfer on the electrode surface.

When solution conductivity drops, the anode can build up a very high charge and then discharge nascent oxygen, then the nascent oxygen can react with the chlorate anion, as described by Bennett and Mack (BM-theory):

$$H_2O \Longrightarrow OH^- + H^+ \Longrightarrow O + 2H^+ + 2e^- \quad (4)$$

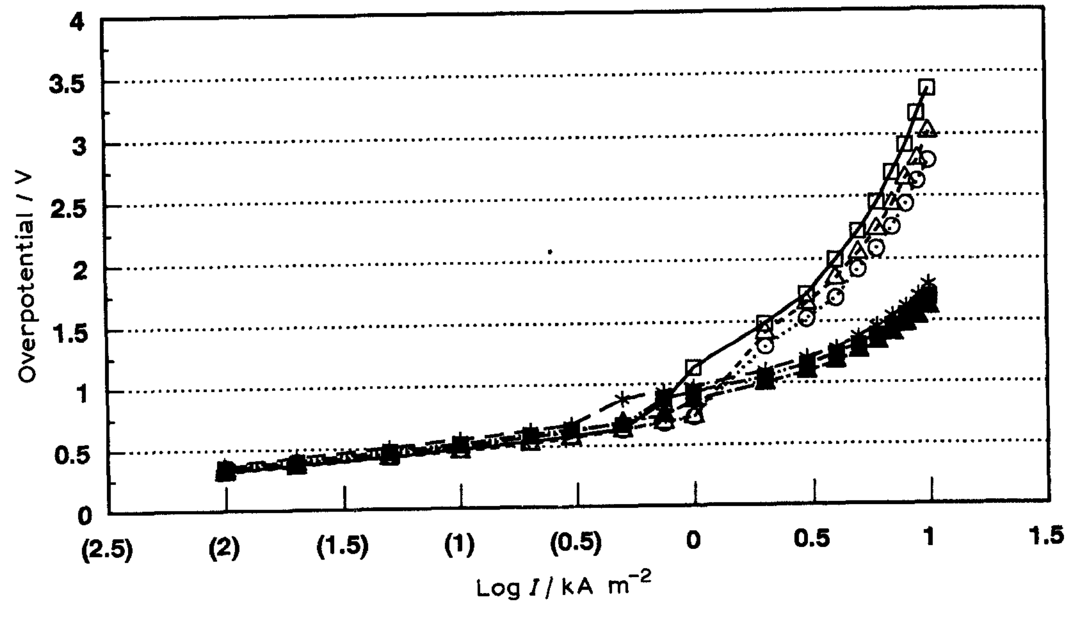

Fig. 7. Anodic overpotential on smooth platinum over niobium: (A) 5% $HClO_3$ at 25, 37 and 50 °C (□, △, ○, respectively); (B) 25% $HClO_3$ at 25, 37 and 50 °C (∗, ■, ▲, respectively).

$$ClO_3^- + H^+ \Longrightarrow HClO_3 \tag{5}$$

$$HClO_3 + O \Longrightarrow HClO_4 \tag{6}$$

The BM–theory, based on the reaction of chlorate with discharged oxygen, is consistent with the lack of variation of current efficiency with pH, but not the high anode potential required to produce perchlorate from chlorate ions.

Knibbs and Palfreeman took exception to Bennett and Mack's theory because of the high anode potential required, and proposed the direct discharge mechanisn of chlorate to perchlorate anions and proposed the following direct discharge mechanism:

$$ClO_3^- \Longrightarrow ClO_3 + e^- \tag{7}$$

$$\begin{aligned} 2ClO_3 &\Longrightarrow O_2Cl\text{–}O\text{–}O\text{–}ClO_2 \\ &\overset{H_2O}{\Longrightarrow} ClO_4^- + ClO_3^- + 2H^+ \end{aligned} \tag{8}$$

$$ClO_3^- \overset{H_2O}{\Longrightarrow} ClO_4^- + 2H^+ + 2e^- \tag{9}$$

Since the generation of ozone produces nascent oxygen, its formation reaction is a good model for the Bennett and Mack model with an E° of 1.501 V, providing an analogue for the high voltage, low conductance and low concentration polarization curves for chlorate and perchlorate. On the other hand, the Knibbs and Palfreeman model would replicate the low voltage pathway, oxidizing the chlorate to perchlorate directly with an E° of 1.189 V as shown by the following reactions:

$$3H_2O \Longrightarrow O_3 + 6H^+ + 6e^- \tag{10}$$

$$E^\circ = 1.501 - 0.0591\,\text{pH} + 0.0098 \log P_{O_3} \tag{11}$$

$$ClO_3^- + H_2O \Longrightarrow ClO_4^- + 2H^+ + 2e^- \tag{12}$$

$$\begin{aligned} E^\circ &= 1.189 - 0.059\,\text{pH} \\ &\quad + 0.0295 \log [(ClO_4^-/ClO_3^-)] \end{aligned} \tag{13}$$

In summary, at low potentials only oxygen is formed at the platinum anode, but at 2.9 V $HClO_4$ is obtained at 60% anode current efficiencies in 6 M concentrations of $HClO_4$.

At higher concentrations the partial current due to $HClO_4$ drops off dramatically due to the adsorption of perchlorate ions on the anode. At low concentrations of chlorate or perchlorate, below 6 M, the rate of oxygen evolution increases when the $HClO_4$ concentration is lowered at constant potential.

2.3. Cell operation data producing perchloric acid

The cell which was used for the perchlorate production tests is shown in Fig. 3. One of the unique features of this two chambered membrane cell is that the anode is spaced from the cathode by a gap of over 0.1 cm, but in order for the cell to operate the cathode must be mounted in intimate contact with the cathode side of the membrane as shown in Fig. 4. This provides for a low energy pathway through the membrane from anode to cathode and continuous, low voltage operations. The catholyte is simply water,, since the conduction pathway is through proton bridging through the ionomeric membrane. Because of a special, somewhat complicated kind of transport of this cation, the proton, found to occur across the charged membrane referred to as 'proton-tunneling'. The 'porous quasi-crystal model'

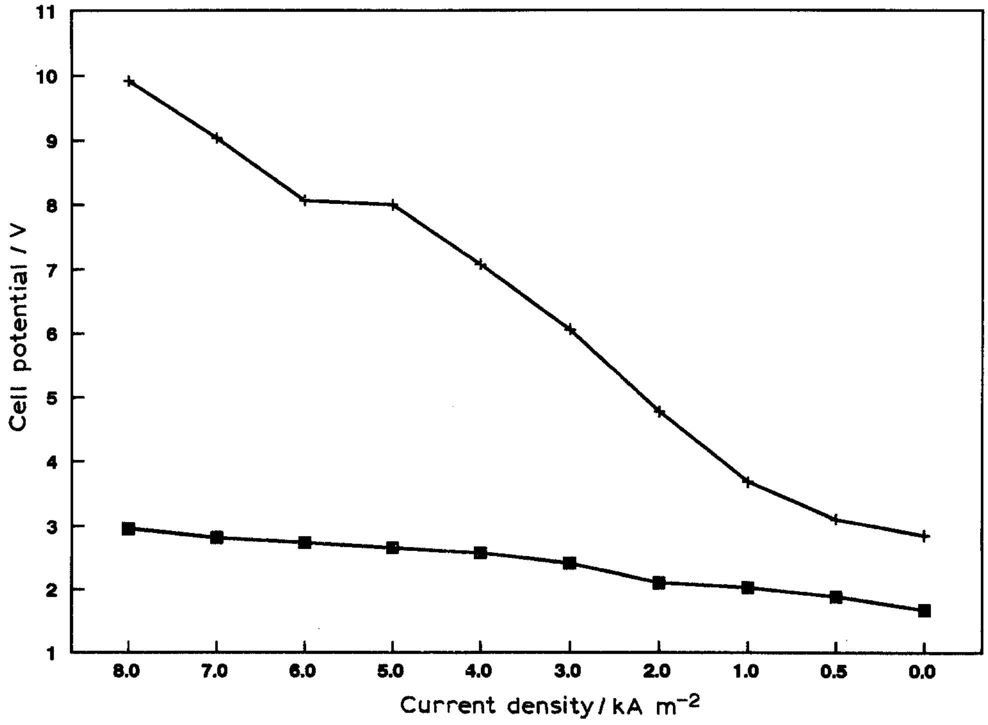

Fig. 8. Polarization run for conversion of chloric to perchloric acid. (■) Anode potential, and (+) total cell voltage.

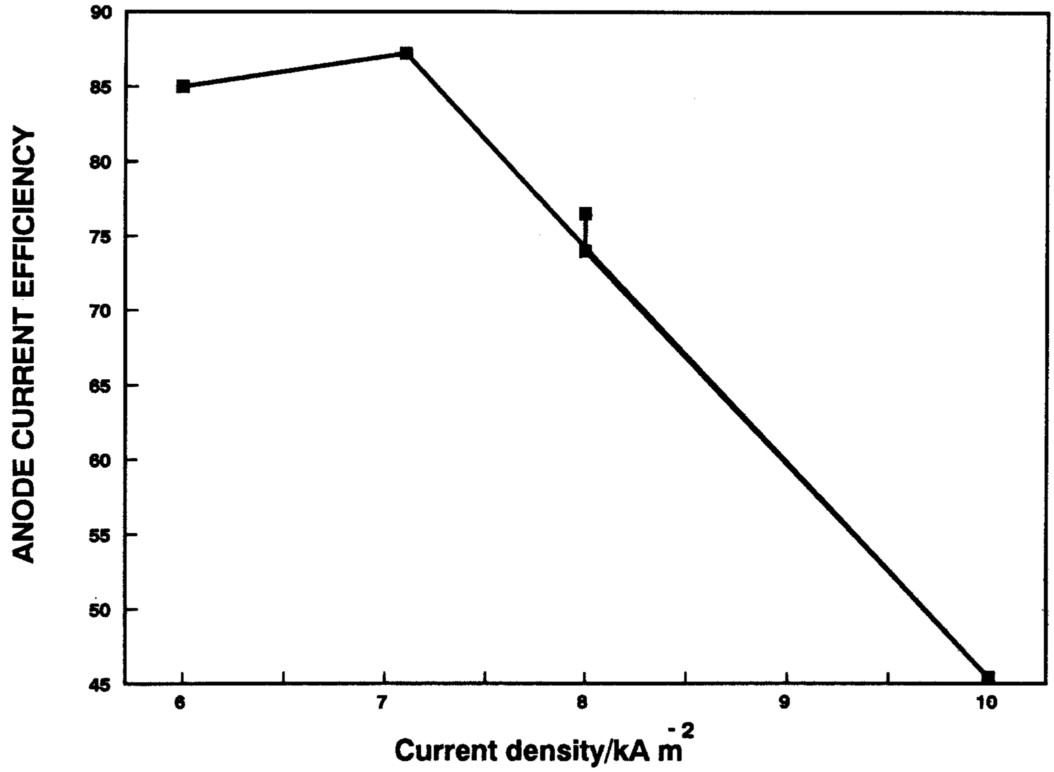

Fig. 9. Current efficiency versus current density for oxidation of ClO_3^- to ClO_4^- at 58 °C.

of Nikolaev, offers some progress in understanding this phenomenon [6].

The dielectric constant of the perfluorinated matrix of the Nafion® membrane is very low and long, flexible pendant groups diffuse locally to enable clusters of the inorganic groups to form. Within the polymer matrix, these groups can become interconnected and thereby reduce the electrostatic free energy of the mass by more than the decrease in the absolute temperature, *T*, times the configuration entropy resulting from the partial segregation. This process provides multiple, low resistance pathways for the proton to tunnel through the polyelectrolyte phase as long as intimate metal-electrode contact is made between cathode and membrane. This arrangement thus provides protons at the anode-membrane interface for tunneling across from anolyte through the membrane and to the cathode metal surface for discharge as hydrogen gas

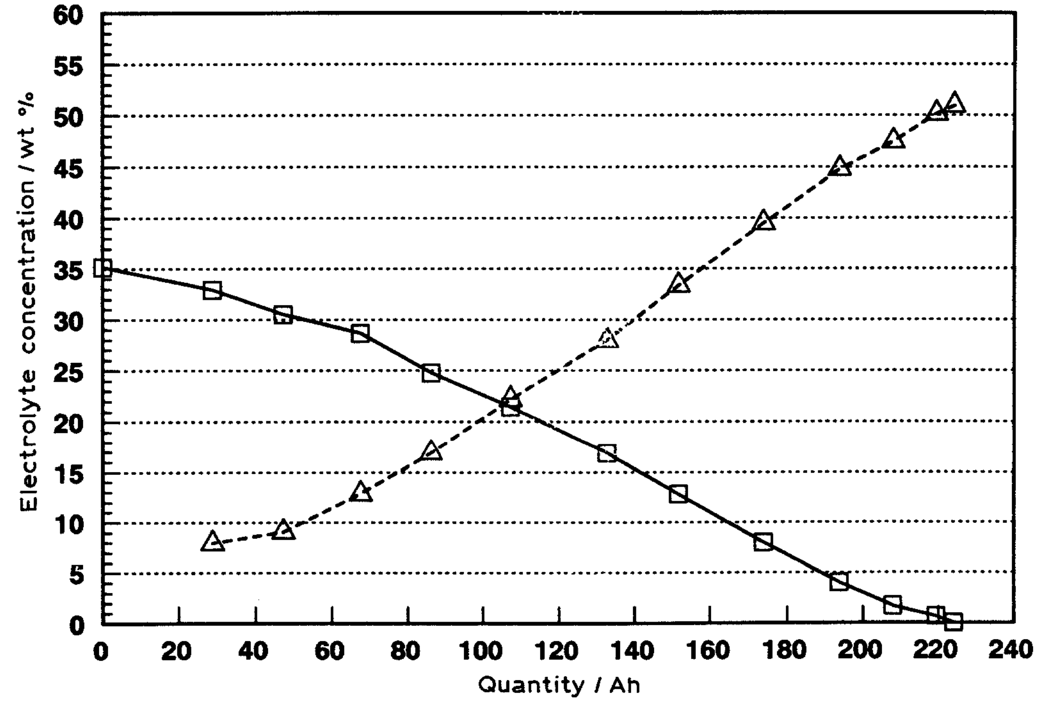

Fig. 10. Performance curves for perchloric acid cell for the oxidation of $HClO_3$ to $HClO_4$. (Current efficiency: 93.36% for 10 kA m^{-2} at 90 °C). (□) %$HClO_3$, (△) %$HClO_4$.

in the open area on the back and side surfaces of the cathode. At the anode membrane-solution interface the proton exchange process is rapid; subsequently the proton moves rapidly across the membrane to the cathode surface only when the three phases, anolyte, polymer, and cathode, remain in intimate contact.

The 20 amp, cathode-membrane sandwich perchloric acid cell with Hastelloy cathode and platinum coated niobium anode was operated at current densitities ranging up to $10\,\mathrm{kA\,m^{-2}}$. Each run lasted from 14 to 25 h, and produced highly pure perchloric acid. Figure 8 shows the anode-solution polarization curves as well as total cell voltage for the conversion of chloric to perchloric acid at 36 °C. The high voltage of the cell has no impact on membrane life. Figure 9 shows the current efficiency against current density for the oxidation of the chlorate. The cell should be operated below $8\,\mathrm{kA\,m^{-2}}$ for best performance. Figure 10 shows the conversion of the chloric acid versus time in hours at $2\,\mathrm{kA\,m^{-2}}$. Complete conversion is achieved in 24 h under these conditions.

The plot of anode efficiencies shows that the highest efficiencies for the perchloric acid will be obtained between 6 and $8\,\mathrm{kA\,m^{-2}}$, where the anode potential is optimum, and anode wear is minimum. The total cell potential, in this case, was in the 8 to 9 V range, with an anode potential of 2.5 to 3 V. At the end of each run virtually all of the detectable chlorate was converted into perchlorate in 25 h.

During some of the runs the random persistence of some of the higher oxides of the halogens were found to appear, such as dichlorine hexoxide. During a typical run, the chloric acid produced from the hypochlorous acid solution from the Olin process becomes converted to a light green liquid, with a dark lemon coloration, that turns water-white at the end of the operation. The visible optical spectrum of this material shows an absorption maximum at 350 nm; thus indicating the presence of Cl_2O_6 causing the coloration. When the colour disappears, indicating the loss of ClO_3^-, and also ClO_3, then so does the colour. The phenomenon can be explained by the following sequence of reactions:

Anode :

$$2ClO_3^- \Longrightarrow 2ClO_3 + 2e^- \qquad (14)$$

Solution:

$$2ClO_3 \Longrightarrow Cl_2O_6, \quad (350\,\mathrm{nm\ band}) \qquad (15)$$

Anode:

$$H_2O \Longrightarrow OH^- + H^+ \Longrightarrow O + 2H^+ + 2e^- \qquad (16)$$

Solution:

$$ClO_3^- + H^+ \Longrightarrow HClO_3 \qquad (17)$$

Solution:

$$HClO_3 + O \Longrightarrow HClO_4 \qquad (18)$$

Dichlorine hexoxide can be formed by the interaction of ClO_2 and O_3, as well as oxidation of the chlorate moiety. In the pure state, Cl_2O_6 is an unstable red oil which freezes at 3.5 °C, with an ionic structure in the solid state of $ClO_2^+ClO_4^-$; however, a strong covalent chlorine-oxygen bond occasionally appears to form under certain conditions causing the colour to persist for longer time periods.

2.4. *Preparation of ammonium perchlorate*

When used as a propellant, the key requirements for ammonium perchlorate are burn rate, product purity and stability. All of these properties of ammonium perchlorate (AP) are affected by the method of preparation. The presence of impurities impact crystal growth, product stability and the overall process economics. Product purity is so important with ammonium perchlorate producers that current commercial processes operate at low efficiencies due to the extensive purification steps involved. Even with this, ammonium perchlorate produced by current technology contains 15–4000 p.p.m. sodium and other metallic impurities in the final product.

Extremely high purity AP can be made directly by reaction of an ammonia compound with aqueous perchloric acid. AP crystals can now be produced which are free of chromium and the transition metals, sulphates and phosphates; as well as being substantially free of alkali metals and chlorides. The starting material, perchloric acid, has been produced by the previously defined electrochemical oxidation of chloric acid in an electrochemical cell having a specially designed cell with an open Hastelloy cathode in intimate contact with the membrane, and a platinum coated niobium anode spaced 0.1 cm from the anode surface of the separator to allow formation of the active chlorine oxide species at the anode surface.

The overall Olin process starts with raw materials of chlorine and caustic soda, as shown in the product tree in Fig. 1. The chlorine gas reacts with the strong caustic in the patented gas-phase Olin process to produce highly pure hypochlorous acid, HOCl, where the chlorine moiety has a charge of plus one. The hypochlorous acid thus formed is next oxidized as a highly concentrated aqueous solution at the anode of the electrochemical cell to form chloric acid, $HClO_3$ [1]. In chloric acid, the chlorine species has a plus five oxidation state. This form of the chlorine oxide can be reduced to +4 by catalytic disproportionation, thus forming chlorine dioxide, ClO_2, or chlorite with chlorine in a +3, state as ClO_2^-. The chloric acid is then transferred to the anode chamber of a second cell. The second cell is the subject of this paper, for after the chloric acid is formed in the first cell, it is subsequently converted into perchloric acid. After the second electrolysis unit operation step is completed and all of the chloric acid is converted to perchloric acid, $HClO_4$, with a plus seven oxidation state on chlorine, the very strong acid is transferred to a second reactor for reaction with a strong ammonium hydroxide solution or with ammonia gas to produce AP.

The starting material, in this case, is perchloric acid and not the usual sodium chlorate with its associated contaminants. The starting material, perchloric acid, has been produced previously by old processes the electrochemical oxidation of alkali metal chlorates in an electrochemical cell without separator between anode and cathode. The chlorate solutions having a pH in the range of 6 to 7, are electrolysed at low temperatures, i.e. 30 to 50 °C, and a current density of $3\,\mathrm{kA\,m^{-2}}$, with a cell voltage of 6.5 to 7 V.

The high purity AP is produced in the Olin process, by introducing the high purity perchloric acid into a crystal reactor after initial electrolysis of the chloric acid. Ammonia and perchloric acid react directly in the reactor and the AP filtered or centrifuged, or spray dried as shown in Fig. 5, with gentle heating. Figure 6 shows the process flow sheet for conversion of chloric to perchloric acid and finally to ammonium perchlorate. In this example, a saturated solution of AP was fed into the spray dryer and cyclone separator and finally deposited as a crystalline powder in the collection chamber with particle size of $50\,\mu m$. The metals analysis shows only 0.02 p.p.m. titanium with all others being nondetectable. This material can be produced as explosive or propellant grade AP, depending on particle size.

3. Conclusions

The following conclusions results from this study:

(i) High purity ammonium perchlorate can be produced in an electrolytic process using no alkali metals through direct electrochemical oxidation of chloric acid, to give ultra-pure perchloric acid.
(ii) Very high purity propellant and explosive ammonium perchlorate can be produced safely after electrolysis by crystallization-drying and spray-drying.
(iii) Both discharge of nascent oxygen and direct discharge of chlorate at the anode appear to occur to explain the electrode kinetics observed in the process.

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