(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040435 A2

(51) International Patent Classification^7: C25B

(21) International Application Number: PCT/EP02/12436

(22) International Filing Date:
7 November 2002 (07.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/344,761 7 November 2001 (07.11.2001) US
10/141,108 8 May 2002 (08.05.2002) US

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(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/040435 A2

(54) **Title:** IMPROVED RHODIUM ELECTROCATALYST AND METHOD OF PREPARATION

(57) **Abstract:** An improved novel rhodium sulphide catalyst for reduction of oxygen in industrial electrolyzers which is highly resistant towards corrosion and poisoning by organic species, thus making it particularly suitable for use in aqueous hydrochloric acid electrolysis, also when technical grade acid containing organic contaminants is employed. By modifying the method of preparation, the activity and consistency of the catalyst is substantially improved.

IMPROVED RHODIUM ELECTROCATALYST AND METHOD OF PREPARATION

STATE OF THE ART

The electrolysis of aqueous HCl solutions is a well known method for the recovery of high-value chlorine gas. Aqueous hydrochloric acid is an abundant chemical by-product, especially in chemical plants making use of chlorine as a reactant: in this case, the chlorine evolved in the anodic compartment of the electrolyser can be recycled as a feedstock to the chemical plant. Electrolysis becomes extremely attractive when the standard hydrogen-evolving cathode is substituted with an oxygen-consuming gas diffusion electrode due to the significant drop in energy consumption. The ability of the gas diffusion electrode to operate successfully in this context is crucially dependent on the nature and performance of the catalyst, and also on the structure of the gas diffusion electrode.

Platinum is generally acknowledged as the most effective catalyst for the electroreduction of oxygen in a wide range of conditions. The activation of gas diffusion electrodes with platinum based catalysts is well known in the art, and finds widespread application in fuel cells and electrolysers of many kinds. However, the case of aqueous HCl electrolysis poses some serious drawbacks to the use of platinum as cathodic catalyst, as it is inevitable for the gas diffusion cathode to come at least partially in contact with the liquid electrolyte, which contains chloride ion and dissolved chlorine. First of all, platinum is susceptible to chloride ion poisoning which negatively affects its activity toward oxygen reduction. A second source of poisoning is constituted by contaminant species, especially organic species, which are in most of the cases dissolved in the by-product hydrochloric acid undergoing electrolysis.

Even more importantly, the combined complexing action of hydrochloric acid and dissolved chlorine gas changes the platinum metal into a soluble salt which is dissolved away, making this material inappropriate for use in gas diffusion electrodes. Furthermore, extremely careful precautions have to be taken during the periodical shut-downs of the electrolysers, otherwise the sudden shift in the cathodic potential, combined with the highly aggressive chemical environment, causes the dissolution of a significant amount of catalyst, and the partial deactivation of the remaining portion. While tailored procedures for planned shut-downs of the electrolysers can be set up for additional costs, little or nothing can he done in the case of a sudden, uncontrolled shut-down due to unpredictable causes like power shortages in the electric network.

Other platinum group metals appear to follow a similar fate. For example, according to Pourbaix' Atlas of Electrochemical Equilibria in Aqueous Solutions, finely divided rhodium metal dissolves in hot concentrated sulphuric acid, aqua regia, and oxygenated hydrochloric acid. Similarly, (hydrated) $Rh_20_3.5H_20$ dissolves readily in HCl and other acids. These problems have been partially mitigated with the disclosure of the rhodium / rhodium oxide based catalyst described in US Patent No. 5,958,197. In particular, the rhodium/rhodium oxide system, although slightly less active than platinum towards oxygen reduction, is not poisoned by chloride ions. Also the chemical resistance to aqueous hydrochloric acid with small amounts of dissolved chlorine is sensibly enhanced with respect to platinum. However, an activation step is needed to obtain a sufficiently active and stable form of this catalyst, and some limitations arise when such a catalyst has to be included in a gas diffusion electrode. For instance, the chemical and electronic state of the catalyst is changed upon sintering in air, a very common step in gas diffusion electrode preparations known in the art. Cumbersome and/or costly operations have to be carried out to replace this step, or to restore the active and stable form of the catalyst afterwards, as disclosed in U.S. Patent 5,958,197. The limitations inherent with the aforementioned rhodium/rhodium oxide were overcome by the novel rhodium sulphide catalyst disclosed in U.S. Patent 6,149,782. We have found that by introducing some changes in the method of preparation, some unexpected gains in performance and consistency are obtained over that disclosed in US Patent 6,149,782.

OBJECTS OF THE INVENTION

It is an object of the invention to provide an improved catalyst for oxygen reduction having desirable and unexpected chemical stability towards highly corrosive media, whereby these improvements are realised through pre-treating the starting materials.

It is another object of the invention to provide an improved catalyst for oxygen reduction having desirable and unexpected electrocatalytic activity in presence of organic contaminants.

It is another object of the invention to provide novel gas diffusion electrodes with the improved catalyst therein having desirable and unexpected electrocatalytic properties, as well as lower and more consistent operating voltages.

It is another object of the invention to provide an electrolytic cell containing a gas diffusion electrode of the invention and to provide an improved method of electrolysing hydrochloric acid to chlorine.

These and other objects and advantages of the invention will become obvious from the following detailed description.

DESCRIPTION OF THE INVENTION

The novel electrochemical catalyst of the invention is comprised of rhodium sulphide, which may be either supported on a conductive inert carrier or unsupported. This catalyst does not require any activation step prior to its use, and surprisingly retains all of its electrocatalytic activity towards oxygen reduction in presence of chloride ions and organic molecules. Moreover, the catalyst is surprisingly not dissolved by the complexing action of aqueous hydrochloric acid - chlorine mixtures, thereby requiring no particular precautions during shut-downs when used in hydrochloric acid electrolyzers.

The catalyst is preferably coated on at least one side of a web, and may be used alone, with a binder, blended with a conductive support and a binder, or supported on a conductive support and combined with a binder. The binder may be hydrophobic or hydrophilic, and the mixture can be coated on one or both sides of the web. The web can be woven or non-woven or made of carbon cloth, carbon paper, or any conductive metal mesh resistant to corrosive electrolytic solutions.

Examples of high surface area supports include graphite, various forms of carbon and other finely divided supports but carbon black is preferred.

Such catalyst coated webs can be employed as gas diffusion cathodes exhibiting cell voltages, current densities and a lifetime that could not be previously obtained under normal operating conditions, especially when used in highly aggressive environments and with low purity reactants, such as the case of electrolysis of by-product hydrochloric acid.

One improvement in the preparation of the catalyst consists in first heating the precursor rhodium chloride at reflux until a steady-state distribution of isomers is obtained. The isomeric distribution of the rhodium chloride is followed with UV/VIS in order to assure steady-state has been obtained. The resulting rhodium sulphide has an improved performance as can be seen by an increase in half-wave potential results.

Another improvement in the electrocatalyst of rhodium sulphide occurs when electrocatalyst is deposited upon carbon black which has been highly dispensed whether or not the rhodium sulphide has been refluxed.

Prior to mixing with the rhodium chloride salt, carbon black is dispersed by high energy mixers. One method is accomplished via a microfluidiser, which is a pressure-driven system and is available through such companies as Microfluidics (Newton, MA, U.S.A.).

Other methodologies use rotor/stator methodology whereby one set of blades is fixed while the another set is spun at high rates around the fixed set. Such action creates high shear on the sample. Rotor/stator operations are often performed in batch mode. Another device is a mill where a spinning barrel with plates performs the function of delivering shear energy to the solution. Kady Company (Scarborough, ME, U.S.A.) provides a range of these machines. These and similar devices are called "homogenizers" and perform the vital function of dispersing solids into solvent in a uniform and consistent manner. The following Example section will describe such a preparation and report results for rhodium sulphide catalyst unanticipated by simple mixing to form a carbon black dispersion.

The best results are obtained with a combination of the two features, namely a single isomer of rhodium chloride deposited on a highly dispersed carbon black resulting in an electrocatalyst with a substantial increase in half-wave potential.

The mixture of refluxed rhodium chloride solution is mixed with the dispersed carbon black, and subjected to a ultrasound step. A rhodium sulphide complex is then prepared upon sparging hydrogen sulphide gas in an aqueous solution of a water-soluble rhodium salt. Nitrogen gas may be used as a carrier for hydrogen sulphide, and a pure nitrogen flow may advantageously be used to purge excess hydrogen sulphide upon completion of the reaction. The resulting solids are recovered by filtration, washing and drying to constant weight at 125°C, for example. The resulting form of rhodium sulphide must be heated in an inert atmosphere at 550 to 650°C, and preferably above 600°C to form a well defined crystalline form of rhodium sulphide catalyst. The heating may be for several hours depending on the size of the batch, and the choice of the temperature is crucial for the formation of a sufficiently stable and active catalyst.

If the temperature is too low, such as 300°C, the resulting crystallites are not well-defined and the catalyst stability is not sufficient. If the temperature is too high, i.e., 725°C, the unsupported catalyst has excellent acid stability but does not possess adequate electrochemical activity.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a typical hydrodynamic voltammogram obtained for a sample of rhodium sulphide catalyst supported on the tip of a Rotating Disk Electrode (RDE) and subjected to a voltage scan. The three-electrode set up employs a saturated calomel reference electrode (SCE) and a platinum wire counter electrode. The solution is 5% HCl, and the test is at room temperature saturated with air. The 1/2 wave position at half plateau height is used as the analytical voltage.

Figure 2 is a schematic of flow system for testing gas diffusion electrodes employed in the generation of Cl_2 from HCl using an oxygen depolarised gas diffusion electrode.

Figure 3 is a plot derived from a series of catalysts prepared using the methods of either Example 1 or Counterexample 1, and incorporated into gas diffusion electrodes of Example 2B. Each catalyst was evaluated using the RDE and then evaluated in a gas diffusion electrode tested in the set-up of Fig 2. The plot compares the analytical voltage from the RDE (El/2) to that obtained in the Lab Cell for the same catalyst.

Figure 4 shows a comparison of 1/2 wave positions for either the counter example 1 catalyst, catalyst prepared with only a reflux of the starting salt, catalyst prepared with only the dispersion of the carbon black and sonication of the mix, and catalyst prepared with a combination of reflux and dispersion/sonication.

Figure 5 is a typical UV/VIS spectrum obtained on solutions of $RhCl_3$ $*nH_20$ immediately upon dissolution and after 2.5 hours of reflux.

In the following examples, there are described several preferred embodiments to illustrate the invention. However, it is to be understood that the invention is not intended to be limited to the specific embodiments.

EXAMPLE 1

A 100 gram batch of rhodium sulphide on carbon is prepared as follows. A quantity of rhodium chloride salt is added to deionised water to make a concentration of Rh metal of about 69 g/l. This solution is refluxed (95-100 deg C) overnight, i.e., about 16 hours. The progress of the reflux is followed with a UV-VIS Spectrum. The ratio of absorption at 470-475 nm to that of 374-380 nm should be in the range of 0.9-1.1, and more preferable 1 when the reflux is complete. Refer to Figure 5 for a typical spectrum obtained after 2.5 hours of reflux.

In a separate operation, mix 64.00g Vulcan XC-72 in 2.0 liters of deionized water placed in a large (about 4 liter) beaker. The mixture is subjected to high-shearing mixing by a Silverson® rotor-stater. The mixture is vigorously agitated in both horizontal and vertical direction at 6500-9000 rpm for 15 minutes. After high-shear mixing, the dispersed carbon mixture is transferred to the vessel with a large stirring bar and 400 mL of 69g/L RhO solution (27.6g Rh metal) is added. Mix the solution on the magnetic stir plate for at least 5 minutes.

Further process the metal and carbon black mixture by placing the vessel in an ultrasonic bath for 20 minutes. Purge the vessel with nitrogen for 30-60 min at a rate of approximately 30 L/hr. Begin bubbling H_2S through the vessel at the desired flow rate, typically about 8-9 liter/hour while the nitrogen continues at 30 L/hr. Five hours after H_2S bubbling starts, a small sample of solution mixture should be taken. It is filtered and Rh concentration checked with XRF or UV-VIS to confirm adsorption of product on the carbon support. Hydrogen sulphide flow is discontinued after confirmation of complete adsorption of product on carbon. The nitrogen purge is continued overnight. On the next day, the catalyst is filtered through a Buchner funnel using a vacuum pump without a wash except for that of a small rinse of the vessel (~30 ml). The filtered intermediate is placed into an oven overnight at a temperature of ~120°C. After drying, a furnace is prepared by purging with argon for 1 hour at room temperature. With continuous inert purge, the temperature of the furnace is ramped from room temperature to 650°C in one hour. The temperature is held at 650°C for 2 hours. After the heater is turned off, the furnace is allowed to cool down in argon to room temperature overnight. once removed from the furnace, the catalyst is analysed and fabricated into a gas diffusion electrode or membrane electrode assembly.

COUNTER EXAMPLE 1

One hundred grams of supported rhodium sulphide were prepared by the following procedure: 57.3 grams of $RhCl_3 \times H_2O$ (39.88% given as rhodium metal) were dissolved in 2 liters of de-ionised (D.I.) water, without any pH adjustment. 53.4 grams of Vulcan XC-72 active carbon were added, and the mixture was slurried with a magnetic stirrer.

Hydrogen sulphide gas was then sparged through the slurry at ambient temperature using nitrogen as a carrier gas. The mixture has been allowed to react as described for 7 hours. Upon completion of the reaction, nitrogen was purged through the system to remove residual H_2S. The remaining solution was vacuum filtered to isolate the solids, which were then washed with de-ionised water and dried at 125°C to a constant weight.

The resulting catalyst cake was finally ground to a fine powder and subjected to 650°C under flowing argon for two hours. A load of catalyst on carbon of 27-28%, given as rhodium metal, was obtained.

EXAMPLE 2

The catalysts of all the above reported examples, along with commercially available platinum on Vulcan XC-72 (for example from E-TEK, Inc.), can be utilised in several different configurations such as listed below. The catalyst of this invention is not limited by the structure of the gas diffusion electrode.

a) ELAT® electrode: A web of carbon cloth with a warp-to-fill ratio of unity and about 25 to 50 yarns per inch, and a 97-99% of carbon content was selected from a commercially available product with a thickness of 10 to 15 mils. Carbon cloth with a thickness of 5 to 50 mils could have advantageously been used for this purpose. A mixture of fluorinated polymer (polytetrafluoroethylene, PTFE, commercialised by DuPont under the trademark Teflon® and Shawinigan Acetylene Black (SAD) carbon, commercialized by Cabot Corp., was coated on each side of the carbon cloth, air drying at room temperature after each coat, until reaching a total loading of 8 to 10 mg/cm^2. A mixture of the powdered catalyst and Teflon® was then applied on one side of the carbon web in multiple coats until obtaining a layer of 0.5 to 2 mg of catalyst per square cm. After the final coat, the carbon cloth was heated to 340°C for 20 minutes.

b) Single-sided ELAT® electrode: The above procedure for preparation of the ELAT® electrode was repeated except the SAB/Teflon® mixture was applied to only one side of the carbon cloth, with a loading of 4 to 5 mg/cm^2. The catalyst coat was applied on the same side, on top of the SAB/Teflon® layer.

c) Flow-through Electrode: A carbon cloth with the same specifications for the ELAT® electrode was selected and 2 to 5 coats of a mixture of catalyst powder and Teflon® were applied to one side thereof. The coated fabric was then heated at 340°C for about 20 minutes to obtain 1.03 mg/cm^2 of rhodium metal. The final heating step or sintering step is believed to melt the Teflon® and distribute it across the carbon catalyst. However, the sintering step may be successfully omitted for this electrode.

d). Membrane Electrode Assembly: An ink was formulated consisting of approximately 3 parts of catalyst and 1 part (as dry weight) of Nafion® ionomer, such as that sold by Solutions Technology, (Mendenhall, Penn., U.S.A.) as a suspension in a mixture of water and lower aliphatic alcohols such as methanol, propanol, and/or butanol. The ink was applied to a Nafion® 324 ion exchange-membrane, comtercialised by DuPont, held in place with a heated vacuum table, via spraying or painting. other ion exchange membranes known in the art may have alternatively been utilised. Subsequent layers of the ink were applied until depositing 0.05 to 1 mg of metal/ mg/cm^2 of catalyst. The assembly was further heated to remove solvents, and assembled with an appropriate electrode backing such as those disclosed in U.S. Patent 6,103,077. The catalyst ink as described could alternatively have been applied to an electrode backing, subsequently heated to remove solvents and assembled with an ion exchange membrane to form an equivalent membrane electrode assembly.

EXAMPLE 3

In order to demonstrate the consistency of the catalyst prepared according to Example 1 and compare multiple batches of catalyst prepared using the improved method to the method of Counterexample 1, the rotating disk electrode (RDE) was employed to obtain electrochemical data independently of laboratory cell testing. A dilute ink of rhodium sulphide on carbon is prepared with by mixing 33mg of supported catalyst with 25 ml iso-propyl alcohol and 25 ml DI water. A total of 1 microliter of this ink is applied in two to three coats onto the tip of a glassy carbon rotating electrode (6mm dia) . Once the ink is dried, an additional layer of 5% Nafion® ionomer solution is applied (10 microliters) and evaporated to dryness. The electrode is placed in a solution of 5% HCl that is at room temperature. A platinum counter electrode and saturated calomel reference electrode (SCE) is connected to a PAR 373 Potentiostat along with the rotating disk electrode. Under various rotation rates, a potential scan is applied whereby a plateau that represents reduction of dissolved oxygen is recorded. The wave potential at one half the plateau height (See Figure 1) is used as the analytical indicator for the catalyst oxygen reduction reaction. The more positive potentials indicate a greater facility for oxygen reduction.

A series of gas diffusion electrodes as described in Example 2B are fabricated with catalysts prepared from the methods of either Example 1 or Counterexample 1. The resulting gas diffusion electrodes are tested using the laboratory test cell as described below. The electrolysis laboratory test is arranged according to the scheme of Fig. 2. The exposed electrode surface area was 100 cm^2 and the membrane was Nafion 324. The anode was titanium mesh activated with ruthenium oxide catalyst. oxygen was fed to the cathode at a rate of up to 2.5-fold stoichiometric excess at ~5 cm water pressure and 13-15% aqueous hydrogen chloride electrolyte was fed to the anode. The electrolyte flow rate was .372 $m^3/hour/cm^2$ at a back-pressure of 200 mbar. Unless stated otherwise, the cell voltages are recorded at 4 kA/m^2 after three days of operation. All voltages were uncorrected for current collector resistance. The temperature of the cell and electrolyte was held at 55°C ± 5°C.

A plot of RDE wave voltage at 1/2 height vs. lab cell voltage is shown in Figure 3. Considering the range of variables stemming from reproducibility of fabrication of the gas diffusion electrode to the statistical reproducibility of a laboratory test cell, the correlation between the wave voltage at 1/2 height and the lab cell voltage indicates the RDE method is very good. As the analytical indicator for RDE moves to positive potentials, the laboratory cell operation voltage decreases. This correlation confirms that the analytical indicator is a relevant measurement for catalyst performance in actual systems.

Multiple batches of catalyst are tested using the RDE methodology, and the average of 15 batches prepared using the counter example 1 method are compared to 10 batches prepared using the method of Example 1. Table 1 summarises the results obtained by the RDE method.

TABLE 1: RDE Peak position at 1/2 plateau height (vs. SCE)

Rhodium sulphide preparation method	Counter Example 1	Example 1	delta
Number of samples	15	10	
Peak Position at half height vs SCE	160 mV	230 mV	70 mV
St. Deviation	24	19	
Rel. St Deviation	15%	8.3%	

This table demonstrates that the improvements of dispersing carbon, refluxing the rhodium salt precursor, and applying ultrasound to the mixture of carbon and metal salt provide an improved catalyst by both performance (average increase in half-wave of 70 mV) and consistency (decrease in relative standard deviation from 15 to 8.3%)

EXAMPLE 4

Catalyst prepared incrementally by either only reflux, or only dispersion (dispersion plus ultrasound) was also tested.

Figure 4 shows the typical improvements possible with each process modification. While applying only the reflux of the starting salt, or only the dispersion of the carbon black clearly shows an improvement, the combination of these additional process steps provides the greatest gain.

Various modifications of the electrocatalyst of the invention may be made without departing from the spirit or scope thereof and it is to be understood that the invention is intended to be limited only as defined in the appended claims.

CLAIMS

1. A rhodium sulphide electrocatalyst formed by heating an aqueous solution of rhodium, salt until a steady state distribution of isomers is obtained and then sparging hydrogen sulphide into the solution to form rhodium sulphide .

2. The catalyst of claim 1 wherein the heating is at reflux.

3. The electrocatalyst of claim 1 supported on a conductive inert carrier.

4. A rhodium sulphide electrocatalyst deposited upon highly dispersed carbon black.

5. The rhodium sulphide electrocatalyst of claim 3 wherein the conductive inert support is highly dispersed carbon black.

6. An electrocatalyst formed by heating an aqueous solution of a rhodium salt until a steady state distribution of isomers is obtained, and then sparging hydrogen sulphide into the solution, deposited upon highly dispersed carbon black.

7. A process for forming an electrocatalyst comprising forming a solution of a soluble rhodium salt, heating the solution to obtain a steady state distribution of rhodium isomers, sparging hydrogen sulphide through the resulting solution to precipitate rhodium sulphide and recovering the same.

8. The process of claim 7 wherein the rhodium sulphide is deposited on highly dispersed carbon black.

9. A membrane electrode assembly with the electrode having a deposit of the electrocatalyst of claim 1 on a conductive inert support.

10. The assembly of claim 9 wherein the support is carbon black.

11. The assembly of claim 10 wherein the carbon black is highly dispersed.

12. In the process of electrolysing hydrochloric acid in an electrolyzer, the improvement comprising using a membrane-electrode assembly of claim 9.

13. In the process of electrolysing hydrochloric acid in an electrolyzer, the improvement comprising using a membrane electrode assembly of claim 11.

14. An electrocatalyst formed by heating an aqueous solution of a rhodium salt until a steady state distribution of isomers is obtained, and then sparging hydrogen sulphide into the solution to form the electrocatalyst.

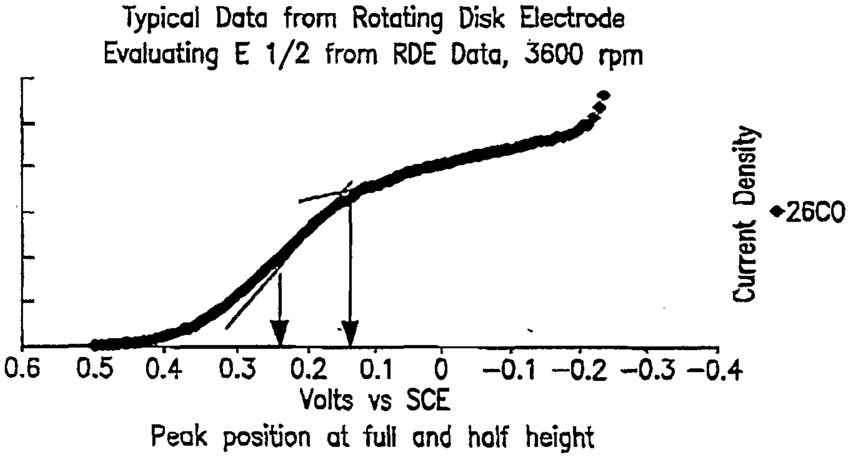
Typical Data from Rotating Disk Electrode
Evaluating E 1/2 from RDE Data, 3600 rpm
Current Density
◆26CO
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
−0.4
Volts vs SCE
Peak position at full and half height

FIG. 1

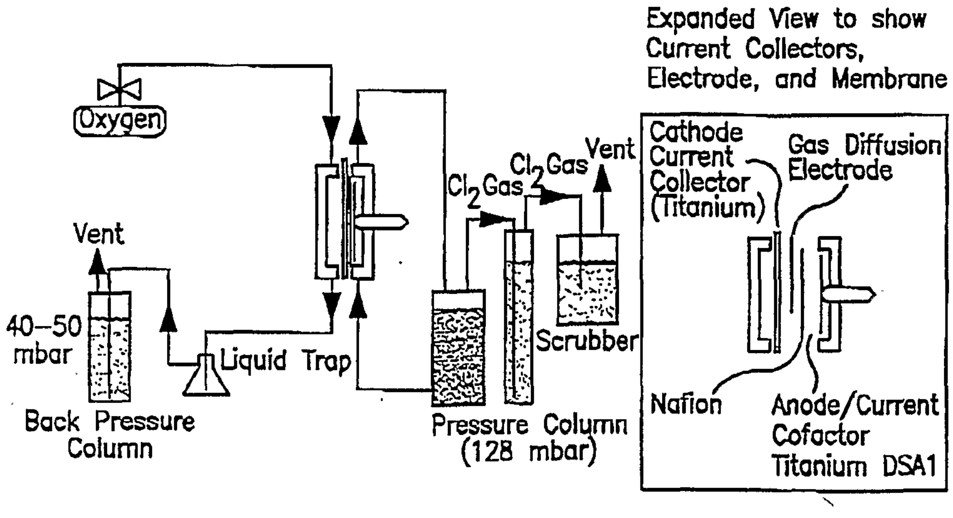
Expanded View to show
Current Collectors,
Electrode, and Membrane
Oxygen
Vent
40–50
mbar
Back Pressure
Column
Liquid Trap
Cl_2 Gas
Cl_2 Gas
Vent
Scrubber
Pressure Column
(128 mbar)
Cathode
Current
Collector
(Titanium)
Gas Diffusion
Electrode
Nafion
Anode/Current
Cofactor
Titanium DSA1

FIG. 2

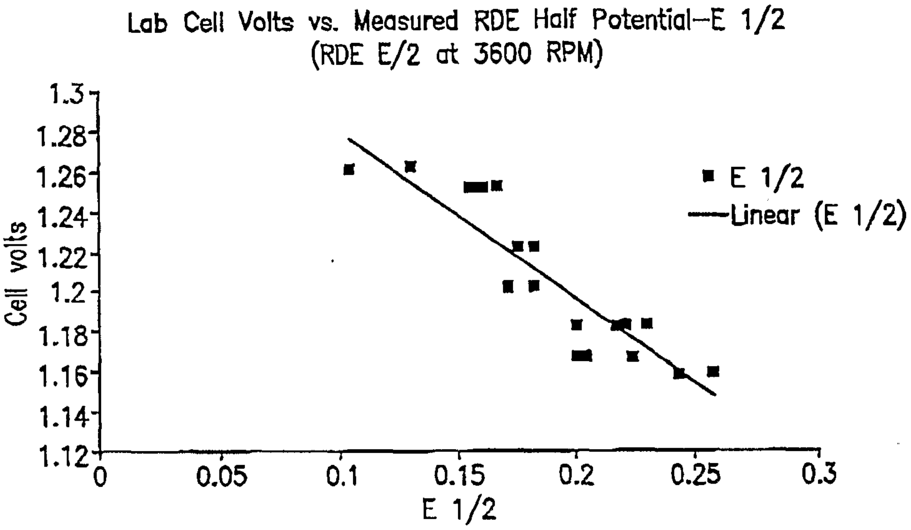
Lab Cell Volts vs. Measured RDE Half Potential–E 1/2
(RDE E/2 at 3600 RPM)
Cell volts
1.3
1.28
1.26
1.24
1.22
1.2
1.18
1.16
1.14
1.12
0
0.05
0.1
0.15
0.2
0.25
0.3
E 1/2
■ E 1/2
—Linear (E 1/2)

FIG. 3

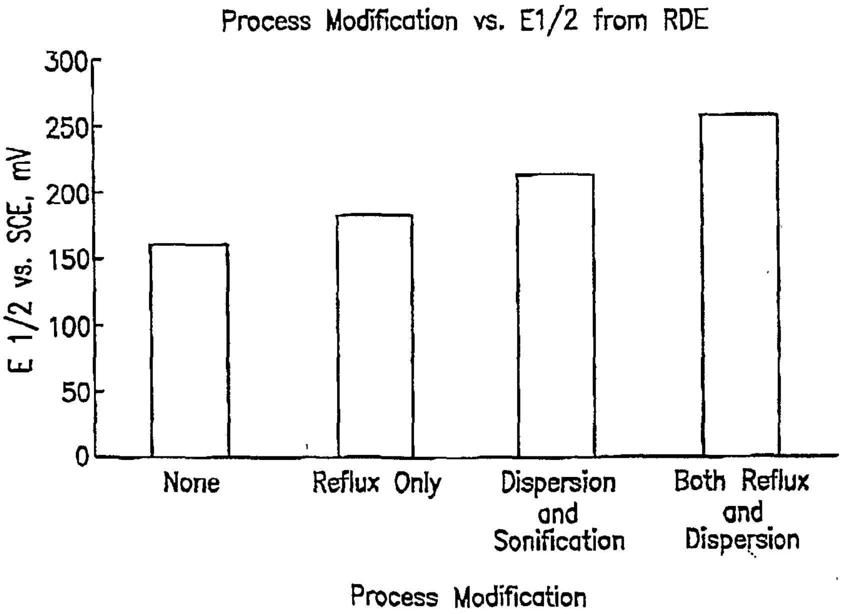
Process Modification vs. E1/2 from RDE
E 1/2 vs. SCE, mV
300
250
200
150
100
50
0
None
Reflux Only
Dispersion and Sonification
Both Reflux and Dispersion
Process Modification

FIG. 4

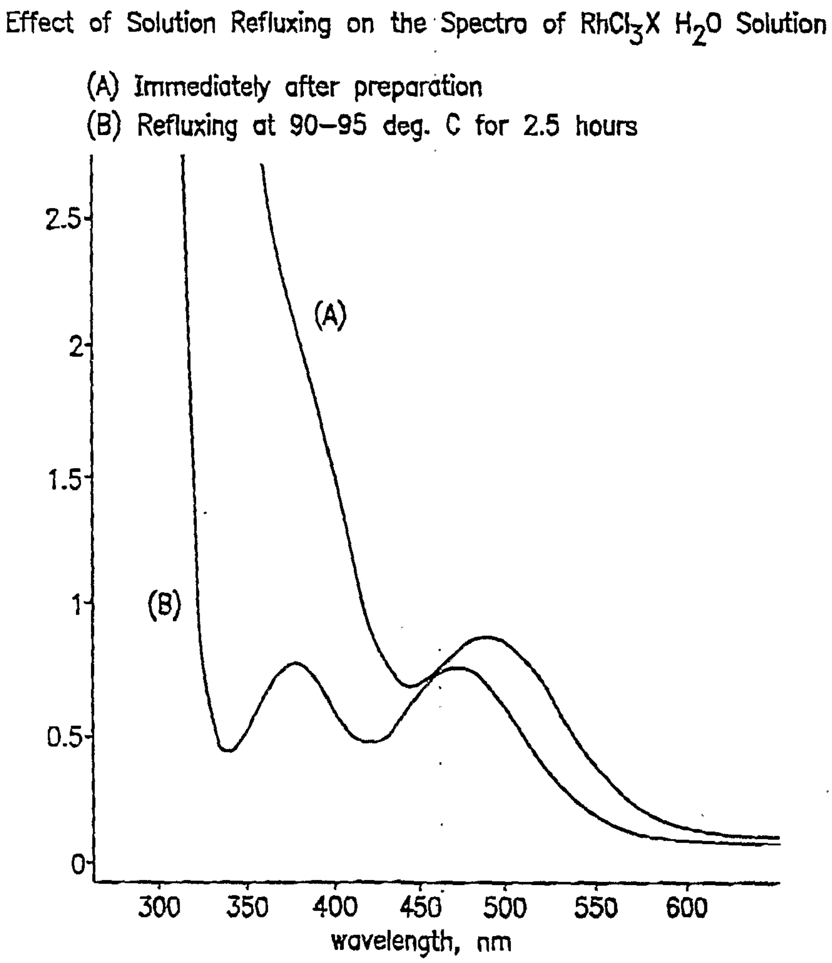
Effect of Solution Refluxing on the Spectro of $RhCl_3X$ H_2O Solution
(A) Immediately after preparation
(B) Refluxing at 90–95 deg. C for 2.5 hours
2.5
2
1.5
1
0.5
0
(A)
(B)
300
350
400
450
500
550
600
wavelength, nm

FIG. 5