AUSTRALIAN PATENT OFFICE
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2

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

AMENDED

~~I~~
We JAPAN METALS AND CHEMICAL COMPANY LIMITED AND
AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY,
of No. 8-4, Koami-cho, Nihonbashi, Chuo-ku,
Tokyo, JAPAN; and No. 3-1, Kasumigaseki 1-chome,
Chiyoda-ku, Tokyo, JAPAN; respectively.

603060

hereby apply for the grant of a Standard Patent for an invention entitled:

"PROCESS FOR PRODUCING ELECTROLYTE FOR REDOX CELL"

which is described in the accompanying ~~provisionaly~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
147684/85	JAPAN	5th July 1985
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LODGED AT SUB-OFFICE
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Melbourne

APPLICATION ACCEPTED AND AMENDMENTS
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The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 3rd day of October 19 86

To: THE COMMISSIONER OF PATENTS

H. W. Rimington
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

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SEE AMENDED APPLICATION

LODGED 3/10/86

hereby apply for the grant of a Standard Patent for an invention entitled:

'PROCESS FOR PRODUCING ELECTROLYTE FOR REDOX CELL"

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which is described in the accompanying complete specification.

Details of basic application(s):—

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REDUCING AND EXTRACTING FE AND CR FROM CHROMIUM ORES FOR ELECTROLYTES

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(56) Prior Art Documents
US 2197146
US 2125642

(57) Claim

1. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in hydrochloric acid to extract iron and chromium, and

separating undissolved residue from the solution thus obtained.

2. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium

.../2

are partially reduced,

dissolving said pre-reduced chromium product in sulfuric acid to extract iron and chromium,

further adding hydrochloric acid thereto, and

separating undissolved residue from the solution thus obtained.

3. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving part of said pre-reduced chromium product in sulfuric acid to extract iron and chromium,

dissolving a further part of said pre-reduced chromium product in hydrochloric acid to extract iron and chromium,

separating undissolved residue from the solutions thus obtained, and

then mixing both solutions.

4. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in a mixture of sulfuric acid and hydrochloric acid to extract iron and chromium, and

separating undissolved residue from the solution thus obtained.

COMMONWEALTH OF AUSTRALIA

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Complete Specification for the invention entitled:

"PROCESS FOR PRODUCING ELECTROLYTE FOR REDOX CELL"

The following statement is a full description of this invention, including the best method of performing it known to us :-

PROCESS FOR PRODUCING ELECTROLYTE FOR REDOX CELL

BACKGROUND OF THE INVENTION

This invention relates to a process for producing both electrolytes for a redox flow cell.

Since electric power can be readily converted into various types of energy and be readily controllable with no known environmental pollution on consumption, the ratio of electric energy consumption to total energy consumption is increasing every year. The problem of supplying electric power resides in its simultaneous production and consumption. It is a requirement of the electric power industry to supply electric power of high quality at constant frequency and voltage while rapidly responding to any variation in power consumption. One solution to this is that the output power is in fact hardly varied, because, for example, a nuclear power plant and a modern coal power plant of high efficiency are operated as high as the rated maximum efficiency, while a hydro-electric power plant adapted to generate in response to the variation in the power consumption is used for an increase in power demand during the day time.

Thus, the night time excess power generated by the nuclear and coal power plants is stored with pumped-hydro electric plants, but the installation conditions of the pumped hydroelectric plants gradually become severe.

From the above mentioned circumstances, various types of secondary battery have been studied for storing electric power without environmental pollution, and redox cells in which two types of redox systems are contacted through an ion exchange membrane have been developed recently.

The principle of this redox cell will be described with reference to Figure 1, which shows an electric power storage system using a 2-tank type redox cell system. In Figure 1, numeral 1 designates a power plant, numeral 2 designates a substation, numeral 3 designates a load, numeral 4 designates an inverter, numeral 5 designates a redox cell system, and the redox cell system 5 is composed of tanks 6, 7 and a flow type electrolytic cell 8.

The electrolytic cell 8, partitioned by an ion exchange membrane 9 is provided therein with an anolyte chamber 10a and a catholyte chamber 10b. The chamber 10a contains an anode 11 and an anolyte such as hydrochloric acid solution including, for example, Fe ions, while the chamber 10b contains a cathode 12 and a catholyte such as hydrochloric acid including, for example, Cr ions. A pump 13a is provided between the tank 6 and the chamber 10a, an anolyte circulation passage 14 is formed between the tank 6 and the chamber 10a. A pump 13b is provided between the tank 7 and the chamber 10b, and a catholyte circulation passage 15 is formed between the tank 7 and the chamber 10b.

In this construction, electric power generated at the power plant 1 and transmitted to the substation 2 is transformed to a proper voltage, and supplied to the load 3.

When excessive power is, on the other hand, produced at night, the power is converted from AC to DC by the inverter 4, and charged in the redox cell system 5.

In this case, the power is charged while circulating the anolyte and the catholyte through the chambers 10a and 10b with the pumps 13a , 13b. When Fe ions are used for the anolyte and Cr ions are used for the catholyte, a reaction in the cell 8 reacts at the charging side of the following formulae (1) to (3):

$$\text{Anode side: } \mathrm{Fe}^{3} + e \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftarrows}} \mathrm{Fe}^{2+} \ldots\ldots (1)$$

$$\text{Cathode Side: } \mathrm{Cr}^{2+} \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftarrows}} \mathrm{Cr}^{3} + e \ldots. (2)$$

$$\text{Total reaction: } \mathrm{Fe}^{3+} + \mathrm{Cr}^{2+} \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftarrows}} \mathrm{Fe}^{2+} + \mathrm{Cr}^{3+} \ldots (3)$$

As described above, the power is stored in the anolyte and the catholyte.

Then, when the supplied power is less than the demand power, the DC power is generated by the reaction at the discharge side of the formulae (1) to (3) while circulating the anolyte and the catholyte through the chambers 10a and 10b. The power is converted from DC to AC by the inverter 4, thus the power is supplied through the substation 2 to the load 3.

The previously proposed power storage system using the redox cells is as described above. Since chromium solution used as a catholyte of the electrolyte of the redox cell has employed electrolytic chromium having 99.5% purity, it is expensive and accordingly a large obstruction to using the redox cells in industry. Thus, a process for dissolving ferrochromium containing chromium and iron in hydrochloric acid and a process for dissolving finely pulverized ferrochromium ore in hydrochloric acid to be employed directly as the electrolytes of the redox cells have been proposed (Japanese Patent Application No. 4183/84).

Further, the process for dissolving the ferrochromium in hydrochloric acid has been also proposed to dissolve the ferrochromium, then to oxidize iron and chromium, to extract chromic chloride ($CrCl_3$) and ferric chloride ($FeCl_3$) in solvent and to refine it (Japanese

Patent Publication No. 37530/82 official gazette, Japanese Patent Laid-open No. 137895/75 official gazette).

The process disclosed in Japanese Patent Application No. 4183/84 dissolves ferrochromium and/or chromium ore in hydrochloric acid and extracts chromium (III) and iron (II).

However, the process has such disadvantages as chromium ore only dissolves slightly in the hydrochloric acid and the solubility of relatively inexpensive high carbon ferrochromium in hydrochloric acid is low so that the process must be done at high temperatures for a long period while low carbon ferrochromium is rather expensive. Another disadvantage is that gas bubbles are generated by the influence of silicon and carbon contained.

Moreover, since low carbon ferrochromium has high hardness and ductility, it can be hardly pulverised to fine particles. Its solubility is superior to the high carbon ferrochromium, but there also arises another disadvantage that the process for pulverizing requires a long period.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for producing the electrolyte for a redox cell.

According to a first aspect of the invention there is provided a process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in hydrochloric acid to extract iron and chromium, and

separating undissolved residue from the solution thus obtained.

Further, according to a second aspect of the invention there is provided a process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in sulfuric acid to extract iron and chromium,

further adding hydrochloric acid thereto, and

separating undissolved residue from the solution thus obtained.

Still further, according to a third aspect of the invention there is provided a process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving part of said pre-reduced chromium product in sulfuric acid to extract iron and chromium,

dissolving a further part of said pre-reduced chromium product in hydrochloric acid to extract iron and chromium,

separating undissolved residue from the solutions thus obtained, and

then mixing both solutions.

Yet still further, according to a fourth aspect of the invention there is provided a process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in a mixture of sulfuric acid and hydrochloric acid to extract iron and chromium, and separating undissolved residue from the solution thus obtained.

Also according to the invention there is provided an electrolyte when produced by the method described in any one of the four immediately preceding paragraphs. The electrolyte may be used in the form of the solution obtained by the process described in any one of said four immediately preceding paragraphs because in a chromium-iron system redox cell iron in the chromium catholyte solution and chromium in the iron anolyte solution do not affect the performance of the cell. However, in a preferred embodiment, iron ions in the solution obtained by said dissolving in HCl, H_2SO_4 or H_2SO_4+HCl are crystallized and separated as part of the undissolved residue and a solution with at least hydrochloric acid therein and with undissolved residue including crystallized iron ions separated therefrom comprises a catholyte, and the separated undissolved residue with crystallized iron ions is dissolved in further hydrochloric acid to produce a further solution comprising an anolyte.

Advantageously, the chromium ore and carbonaceous reducing agent are agglomerated (formed into pellets) prior to said partial reduction, and most advantageously the pre-reduced carbon product is dissolved in the form of a powder.

The pre-reducing heating step may advantageously be performed at a temperature in the range 1200-1400°C.

BRIEF DESCRIPTION OF THE DRAWINGS

Various embodiments of a process in accordance with the invention will now be described by way of example only with reference to the Examples and to the accompanying drawings, in which:

Figure 1 is an explanatory view of a power storage system using redox cells;

Figure 2 is a view showing the relationship between the sulfuric acid concentration (M) and the hydrochloric acid concentration (M) and the internal resistance of the cell; and

Figure 3 is a diagram showing a solubility curve of Fe^{2+} in 3M hydrochloric acid and 5M hydrochloric acid solution in 1M chromium chloride coexistence.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The pre-reduced chromium product used in the process of this invention is, for example, a raw material for producing a ferrochromium such as powder ore indicated in Table 1 to be mixed with carbon material of 110 to 150% of theoretical amount required for reducing iron oxide and chromium oxide in the chromium ore, added with a binder, and pelletized (having 6 to 12 mm particle size), and reduced in a rotary kiln at 1200 to 1400°C.

This is hereinafter referred to as "pre-reduced chromium pellet". An example of the composition of the pre-reduced chromium pellet is illustrated in Table 2.

TABLE 1

Production area of ore	Composition (wt%)				
	Cr_2O_3	FeO	SiO_2	Al_2O_3	MgO
South Africa	45.0	25.0	2.5	12.0	10.0
Madagascar	50.5	17.3	3.2	14.0	11.0
India	51.8	15.7	5.9	10.2	11.3

TABLE 2 (Unit: wt%)

T·Cr	M·Cr	T·Fe	M·Fe	SiO_2	Al_2O_3	MgO
30.0	18.0	15.2	14.4	10.0	13.2	13.0

(note): T·Cr and T·Fe are all chromium and all iron, respectively, and M·Cr and M·Fe are all metallic chromium and metallic iron, respectively.

As apparent from Table 2, the iron and the chromium contained in the pre-reduced chromium pellet are mixed mainly with metallic iron and metallic chromium as well as unreduced iron oxide and chromium oxide.

When the pre-reduced chromium pellet is dissolved in hydrochloric acid, the contained metallic chromium reacts with the hydrochloric acid to be dissolved to produce chromium (III) ions.

However, when the pellet is dissolved in hydrochloric acid, not all of the metallic iron and metallic chromium are dissolved but remain partly undissolved according to the dissolving conditions (concentration of hydrochloric acid, dissolving temperature and dissolving time, etc.). The undissolved residue may be separated prior to using the electrolyte solution.

As described above, the pre-reduced chromium pellet can be dissolved in hydrochloric acid, but the extractions of the metallic iron and the metallic chromium are not complete, and a relatively long time is required. On the other hand, when the metallic iron and the metallic chromium in the pre-reduced chromium pellet are treated in sulfuric acid, they are almost completely dissolved and extracted in a short time. However, for redox cells using iron ions and chromium ions chloride ions must coexist in the electrolyte. Thus, when the pre-reduced product is dissolved in sulfuric acid, it is necessary to add hydrochloric acid. This is because the ions for electrode reaction in the anolyte and catholyte of the redox cells are iron and chromium chloride complex ions. Undissolved residue may be separated from the resultant solution prior to use as an electrolyte.

The metallic chromium contained when the pre-reduced chromium pellet is dissolved only in sulfuric acid is reacted and dissolved according to the following formula (4) to produce chromium (III) hexa aqua complex ions.

$$Cr + 3H_2SO_4 \rightarrow Cr(H_2O)_6^{3+} + 3SO_4^{2-} + 3H^+ + 3/2H_2\uparrow \quad ....(4)$$

The ions produced by dissolving the pre-reduced chromium pellet differ according to whether it is dissolved only in hydrochloric acid or only in sulfuric acid.

When the pre-reduced chromium pellet is dissolved in hydrochloric acid, chromium (III) chloride complex ions are produced according to the following formula (5):

$$Cr + 8HCl \rightarrow CrCl(H_2O)_5^{2+} + 7HCl + 5H^+ + 3/2H_2\uparrow \quad .....(5)$$

The redox potentials of the above two chromium complex ions are different, and the redox potentials are sequentially shifted to the negative side in the order of chromium (III) chloride complex ions and chromium (III) hexa aqua complex ions.

The electrode reactivity of the chromium (III) hexa aqua complex ion is lower than that of the chromium (III) chloride complex ion. Since the redox potential of the chromium (III) hexa aqua complex ions produced by the dissolving in sulfuric acid is near the hydrogen production potential, hydrogen is readily produced in the charging reaction of the cells which causes the cell efficiency to decrease. Therefore, it is desirable to use as the reactant the chromium (III) chloride complex ions (having fast electrode reaction rate) because it has a reduced reaction resistance and its redox potential is spaced from the hydrogen production potential.

For the abovementioned reasons, the inventors of the present invention have further studied to discover the process for producing electrolytes for the redox cells which has the steps of dissolving respective parts of the pre-reduced chromium product in sulfuric acid and hydrochloric acid to extract iron and chromium, then mixing the resultant solutions to contain chromium (III) chloride complex ions in the solutions after separating undissolved residue.

The mixed solution can readily convert the chromium (III) hexa aqua complex ions produced by dissolving in sulfuric acid into chromium (III) chloride complex ions for charging and discharging. In other words, coexistent chromium (II) complex ions perform a catalytic role to simply convert the chromium (III) hexa aqua complex ions into chromium (III) chloride complex ions. Further, the mixed solution can also prevent the solubility of the iron and chromium from decreasing due to the common ion effects which may arise when solely using hydrochloric acid, thereby reducing the volume of the tank of the cell system.

However, most chromium (III) complex ions are slow in the ligand substituting reaction, requiring several months for the chromium (III) hexa aqua complex ions produced by dissolving in sulfuric acid to change to chloride complex ions, even if hydrochloric acid is added later. Further, when dissolved only in hydrochloric acid, a large quantity of hydrochloric acid coexists, and the solubility of the iron ions and chromium ions decreases by the common ion effect of the chloride ions.

Inventors of the present inventions have therefore further studied to result in dissolving the pre-reduced chromium product in a mixture of sulfuric acid and hydrochloric acid, thereby obtaining the electrolytes further adaptive for the electrolytes in the redox cells after undissolved residues have been separated from the resultant solution. When the pre-reduced chromium product is dissolved in the mixed acid as described above, partial chromium which is hardly dissolved in hydrochloric acid can be dissolved in sulfuric acid to produce chromium (III) chloride complex ions by coexistent hydrochloric acid.

In addition, when the pre-reduced chromium product is dissolved in the mixture of sulfuric acid and hydrochloric acid, another effect of reducing the internal resistance of the cell can be attained.

In other words, the internal resistance of the redox cell is determined by the resistance of the cation membrane through which ions (hydrogen ions) are mainly passed and the electrode reaction resistance of the reactant due to the electrode reaction. Then, if the mixed acid concentration dependency of the both resistances is obtained, the optimum mixed acid concentration for minimizing the internal resistance can be determined. The dissolving amount of chromium is larger in the mixture acid as compared with that only in hydrochloric acid since its coexistent ion effect is smaller. When dissolved only in hydrochloric acid, if the hydrochloric acid concentration is reduced to increase the solubility, the resistance of the cation exchange membrane used as membrane of the cell increases. Then, it is necessary to increase the solubility by decreasing the chloride ion concentration, and to reduce the membrane resistance with coexisting sulfuric acid and raising the hydrogen ion concentration. From this point of view. it is effective to dissolve in mixed acid as described above. Then, the results of discussing the mixed acid range for satisfying both the reduction of the internal resistance and increasing the solubility are shown in Figure 2. It is understood from Figure 2 that the cell resistances are almost constant in the mixed acid of 2-4M hydrochloric acid and 1-3M sulfuric acid except 1M hydrochloric acid. The 1M hydrochloric acid is less and 2M or more hydrochloric acid is necessary from the standpoint of reducing the internal resistance. The sulfuric acid is preferably 2M or more.

As evident from the above descript
hydrochloric acid in the solutions co

production of chromium complex ions of reactive substance, and the sulfuric acid contributes to the reduction in the membrane resistance, the improvement in the solubility of the chromium, and complete dissolving of the chromium metal in the pre-reduced chromium pellet. Then, the acids are advantageous to be used in the above concentration ranges.

The concentrations of the chromium ions and iron ions in the solutions may be regulated to become 0.5 to 2M, more preferably 1 to 2M, and the hydrochloric acid concentration is preferably 2 to 6M.

In the redox cell of chromium-iron system, iron in chromium solution of catholyte and chromium in iron solution of anolyte do not affect the cell performance.

However, it is advantageous in industry to separate the mixed solutions of the iron and the chromium obtained by dissolving the pre-reduced chromium pellet, and, as the process for separating the ions, a crystallizing treatment utilizing the temperature dependence of the solubility of iron chloride (II) is effective.

Figure 3 shows the relationship between the temperature and the solubility of Fe^{2+}. For example, the solution which contains 5M hydrochloric acid (5M HCl) and 1M $CrCl_3$ dissolves approx. 2M of Fe^{2+} at 60°C, but when this solution is cooled to 20°C, it becomes approx. 0.8M, and the remaining 1.2M is crystallized to be precipitated and separated as part of the undissolved residue.

Therefore, a part of the iron ions in the chromium solution of catholyte can be removed simply by this process. Further, the crystallized and removed iron chloride can be dissolved in hydrochloric acid and used as anolyte.

As described above, a pre-reduced chromium pellet of a raw material for producing a ferrochromium is used to produce the electrolytes for the redox cells by dissolving the metallic iron and the metallic chromium existing in the pre-reduced chromium pellet in the hydrochloric acid with or without sulfuric acid, and producing Fe^{2+} when the metallic iron and metallic chromium are dissolved, thereby simply obtaining Fe^{2+} and Cr^{3+} necessary for the electrolytes of discharging state.

Further, any undissolved residue can be reused as a raw material for producing the pre-reduced chromium pellet, and pulverization of the pre-reduced chromium products is more simple than ferrochromium, thereby providing good workability and accordingly improving the treating efficiency to reduce the cost.

Examples of this invention will now be described.

EXAMPLE 1

The composition of pre-reduced chromium pellets used in these Examples and the reducing ratio of iron and chromium are listed in Table 3.

TABLE 3 (Composition: wt%)

T·Cr	T·Fe	SiO_2	Al_2O_3	MgO	M·Cr	M·Fe	Cr reduction ratio (%)	Fe reduction ratio (%)
31.6	16.3	5.6	13.5	12.8	18.7	15.1	59.2	92.6

After the pre-reduced chromium pellet was pulverized to approx. 60 mesh or smaller, 1.8 liter of 10M hydrochloric acid was added to 1Kg of the powder, the mixture was then heated to approx. 80°C, and extracted for 12 hours.

Then, the treating solution was cooled to room temperature, and undissolved residue was filtered and separated. This residue contained ferric chloride which was automatically crystallized by cooling it. The solution composition after undissolved residue was separated is as in Table 4, and this was used directly as a catholyte.

Further, 0.8 liter of 3M hydrochloric acid was added to the undissolved residue filtered by the previous step to dissolve the ferric chloride previously crystallized, the undissolved residue was then filtered ~~and obtained~~ leaving a solution shown in Table 5, which was ~~and~~ used directly as an anolyte.

TABLE 4

Cr		Fe		HCl concentration
g/l	M	g/l	M	M
67.44	1.30	37.2	0.67	3.2

TABLE 5

Cr		Fe		HCl concentration
g/l	M	g/l	M	M
6.25	0.12	93.75	1.68	3.0

The extraction ratio of Cr and Fe in the pre-reduced chromium pellet of the raw material in the abovementioned dissolving step are 38.3 and 85.3% for T·Cr and T·Fe, and 64.7% and 92.1% for M·Cr and M·Fe in the pre-reduced chromium pellet.

EXAMPLE 2

2 liters of 9M sulfuric acid was added to 1Kg of the same pre-reduced chromium pellet powder as in the EXAMPLE 1, heated at 80°C, and extracted for 2 hours.

After the undissolved residue was filtered and separated, 1Kg of pre-reduced chromium pellet powder and 1.6 liter of 10M HCl were added to the solution, and again heated under the same conditions, and extracted.

The compositions of the first solution and the second solution are as in Table 6.

TABLE 6

	Cr		Fe		HCl	H_2SO_4
	g/l	M	g/l	M	M	M
First solution	91.6	1.76	75.26	1.35	0	5.01
Second solution	103.2	1.98	85.29	1.53	4.57	0.94

Then, the second solution was cooled to room temperature, and iron chloride crystallized together with the undissolved residue was filtered and separated. The composition of the solution as a result is as shown in Table 7, and this was used directly as a catholyte.

TABLE 7

Cr		Fe		HCl	H_2SO_4
g/l	M	g/l	M	M	M
101.5	1.98	41.9	0.75	4.57	0.94

0.5 liter of 4M hydrochloric acid was added to the residue filtered in the same manner as the EXAMPLE 1, the crystallized product was dissolved, the undissolved residue was filtered and separated to obtain solution shown in

Table 8 as an anolyte.

TABLE 8

Cr		Fe		HCl	H_2SO_4
g/l	M	g/l	M	M	M
14.0	0.27	85.0	1.52	4.0	0.1 or less

In the above dissolving steps, the extraction ratios of the metallic iron and the metallic chromium in the pre-reduced chromium pellet are approx. 100% in the first dissolving step, and in the second dissolving step, 67% of the metallic chromium and 85% of metallic iron. The pre-reduced chromium pellet after the second dissolving step retains undissolved metallic iron and metallic chromium, but substantially all may be extracted by using the residue in the first dissolving step for producing subsequent electrolyte.

As a result that the solutions produced in the EXAMPLES 1 and 2 is used as the electrolytes in the redox cells, the result shown in Table 9 is obtained, and no apparent difference is obtained in the power efficiency from the case when the electrolytes are derived from ferrochromium.

TABLE 9 (Cell performance by electrolyte obtained according to Example 1 or Example 2)

Current density (mA/cm^2)	charging rate %	current efficiency %
20	78.5	96.1

EXAMPLE 3

After the pre-reduced chromium pellet having the same composition as that in the EXAMPLE 1 was pulverized to approx. 60 mesh or smaller, 2.0 liters of 10M hydrochloric acid was added to 1Kg. of the powder, heated approx. $80^{\circ}C$, and extracted for 12 hours.

Then, after the solution was cooled to room temperature, the undissolved residue was filtered and separated. The residue contained iron (II) chloride which is automatically crystallized by cooling. The solution composition after the undissolved residue was separated is shown in Table 10.

TABLE 10

Cr		Fe		HCl
g/l	M	g/l	M	M
63.0	1.21	35.7	0.64	4.0

In addition, 1.0 liter of 9M sulfuric acid was added to a furthur 0.5Kg of the pre-reduced chromium pellet powder, heated at approx. $80^{\circ}C$, and extracted for 2 hours. Then, after the solution was cooled to room temperature, the undissolved residue was filtered and separated. The solution composition after separation is shown in Table 11.

TABLE 11

Cr		Fe		H_2SO_4
g/l	M	g/l	M	M
86.5	1.66	69.4	1.24	5.27

Then, the solution treated with hydrochloric acid, the solution treated with sulfuric acid and water were mixed at the ratio of 7 : 2 : 1 as a catholyte.

Further, that mixed solution of 0.3 liter of 10M hydrochloric acid, 0.2 liter of 9M sulfuric acid and 0.5 liter of water was added to the undissolved residue which was treated with hydrochliric acid. When the mixed solution was heated, iron(II) chloride crystallized previously was dissolved, and the undissolved residue was further filtered and separated to obtain solution used as an anolyte.

The compositions of the electrolytes thus obtained are listed in Table 12.

TABLE 12

	Cr		Fe		HCl	H_2SO_4
	g/l	M	g/l	M	M	M
Catholyte	61.4	1.18	38.9	0.70	2.8	1.80
Anolyte	6.9	0.12	61.5	1.10	3.0	1.85

The extraction ratios of the metallic chromium and the metallic iron in the pre-reduced chromium pellet of the raw material in the abovementioned dissolving step are 67.4%,86.0% in case of the hydrochloric acid, and 92.5%, 91.9% in case of the sulfuric acid, and the metallic chromium as a whole is 75.8% and the metallic iron is 88.8%.

Further, the cell performance of the case that the electrolytes obtained in the above treatment are used are 1.60 ohm cm^2 of the internal resistance being low, and 98.5% of current efficiency being preferable.

EXAMPLE 4

1 liter of mixed acid obtained by mixing 9M sulfuric

acid and 10M hydrochloric acid at 1 : 2 was added to 0.5Kg of the same pre-reduced chromium pellet as that in the EXAMPLE 1, heated at approx. 80°C, and extracted for 4 hours.

Then, the solution was cooled to room temperature to crystallize part of the iron(II) chloride, and filtered and separated together with undissolved residue.

Then, to regulate the acid concentration, 0.4 liter of 10M hydrochloric acid was added to the solution screened and separated from the undissolved residue, water was added to 1.5 liter in the entire amount as a catholyte.

Further, 0.2 liter of 10M hydrochloric acid, 0.15 liter of 9M sulfuric acid and 0.35 liter of water were added to the undissolved residue filtered by the previous treatment, heated, the iron (II) chloride crystallized previously was dissolved, and the undissolved residue was then filtered and separated to obtain solution used as an anolyte.

The compositions of the solutions are listed in Table 13.

TABLE 13

	Cr		Fe		HCl	H_2SO_4
	g/l	M	g/l	M	M	M
Catholyte	52.6	1.01	20.6	0.37	2.1	1.90
Anolyte	5.9	0.11	60.2	1.08	2.1	1.95

The extraction ratios of the metallic chromium and the metallic iron in the pre-reduced chromium pellet of the raw material in the abovementioned dissolving step are

88.8%, 96.7%, and the cell perormance of the obtained electrolytes is 1.58 ohm cm^2 of the internal resistance, and 99.0% of current efficiency.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in hydrochloric acid to extract iron and chromium, and

separating undissolved residue from the solution thus obtained.

2. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in sulfuric acid to extract iron and chromium,

further adding hydrochloric acid thereto, and

separating undissolved residue from the solution thus obtained.

3. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving part of said pre-reduced chromium product in sulfuric acid to extract iron and chromium,

dissolving a further part of said pre-reduced chromium product in hydrochloric acid to extract iron and chromium,

separating undissolved residue from the solutions thus obtained, and

then mixing both solutions.

4. A process for producing an electrolyte for a redox cell which comprises the steps of

heating iron-containing chromium ore together with carbonaceous reducing agent to produce a pre-reduced chromium product in which both the iron and the chromium are partially reduced,

dissolving said pre-reduced chromium product in a mixture of sulfuric acid and hydrochloric acid to extract iron and chromium, and

separating undissolved residue from the solution thus obtained.

5. The process according to Claim 4, wherein the concentrations of hydrochloric acid and sulfuric acid in the mixture are in the ranges of 2 to 4M of hydrochloric acid and 1 to 3M of sulfuric acid.

6. The process according to any one of Claims 1 to 5, wherein the chromium ore and carbonaceous reducing agent are formed into pellets prior to said partial reduction.

7. A process according to any one of Claims 1 to 6 wherein the pre-reduced chromium product is dissolved in the form of a powder.

8. A process according to any one of Claims 1 to 7 wherein the pre-reducing heating step is performed at a temperature in the range 1200-1400°C.

9. The process according to any one of Claims 1 to 8, wherein the concentrations of chromium ions and iron ions in the solution obtained by said dissolving with at least hydrochloric acid are regulated to 1 to 2M each, and the concentration of hydrochloric acid in said solution is 2

to 6M.

10. The process according to any one of Claims 1 to 9, wherein iron ions in the solution obtained by said dissolving in HCl, H_2SO_4 or H_2SO_4+HCl are crystallized and separated as part of the undissolved residue.

11. A process according to Claim 10 wherein the solution with at least hydrochloric acid therein and with undissolved residue including crystallized iron ions separated therefrom comprises a catholyte, and wherein said separated undissolved residue including crystallized iron ions is dissolved in further hydrochloric acid to produce a further solution comprising an anolyte.

12. A process for producing an anolyte and a catholyte for a redox cell substantially as hereinbefore described with reference to any one of the Examples.

13. A process for producing an electrolyte according to any one of Claims 1 to 4 and substantially as hereinbefore described with reference to Figures 2 and 3 of the accompanying drawings.

14. An electrolyte when produced by the process claimed in any one of the preceding claims.

DATED this 14th day of August, 1990.

JAPAN METALS AND CHEMICAL COMPANY LIMITED AND
AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY
By their Patent Attorneys
DAVIES & COLLISON

Fig. 1

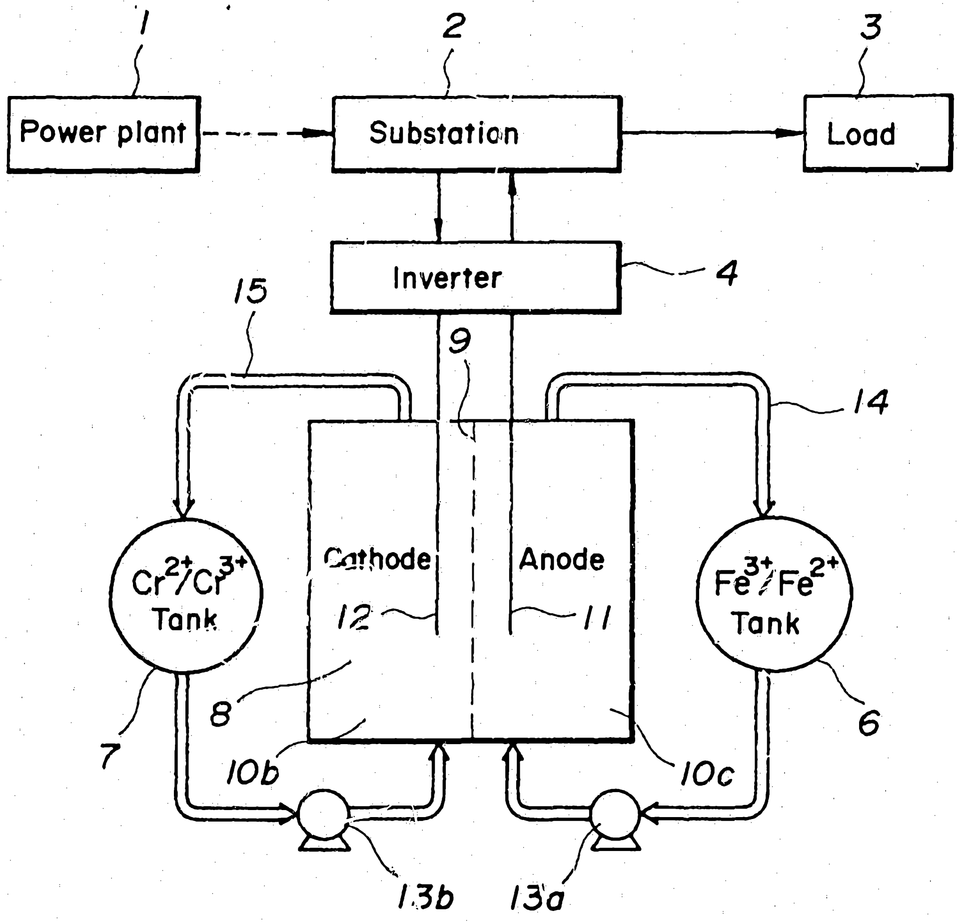
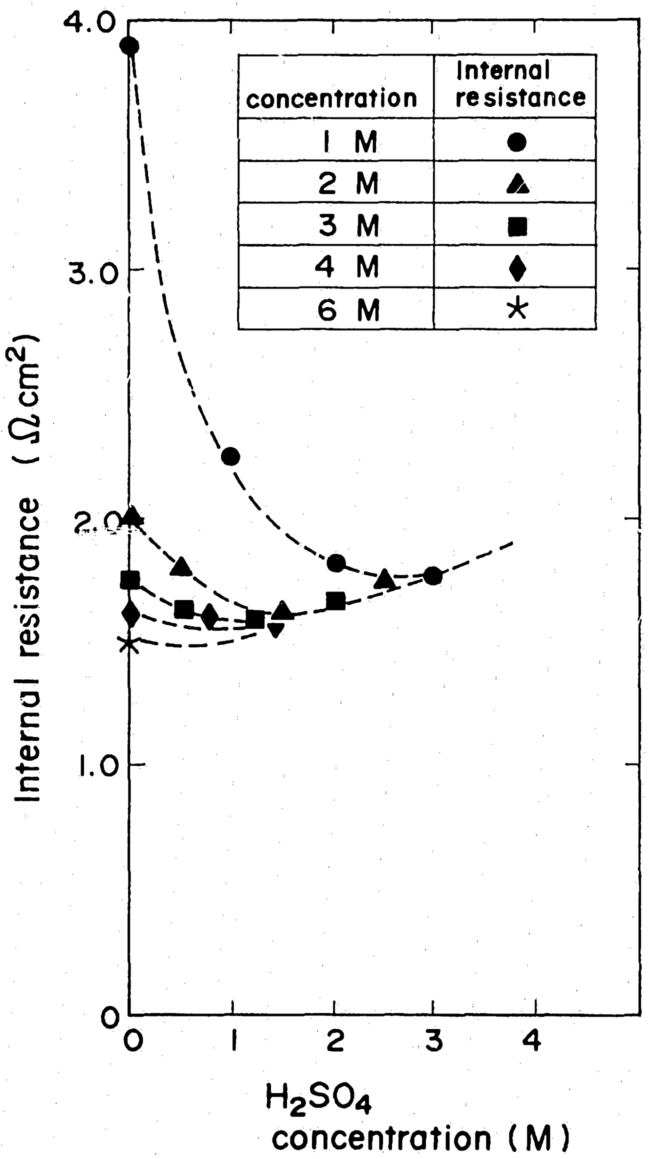

1
2
3
Power plant
Substation
Load
Inverter
4
15
9
14
Cathode
Anode
Cr^{2+}/Cr^{3+} Tank
Fe^{3+}/Fe^{2+} Tank
12
11
8
7
6
10b
10c
13b
13a

Fig. 2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3.0
2.0
1.0
0
Internal resistance (Ωcm²)
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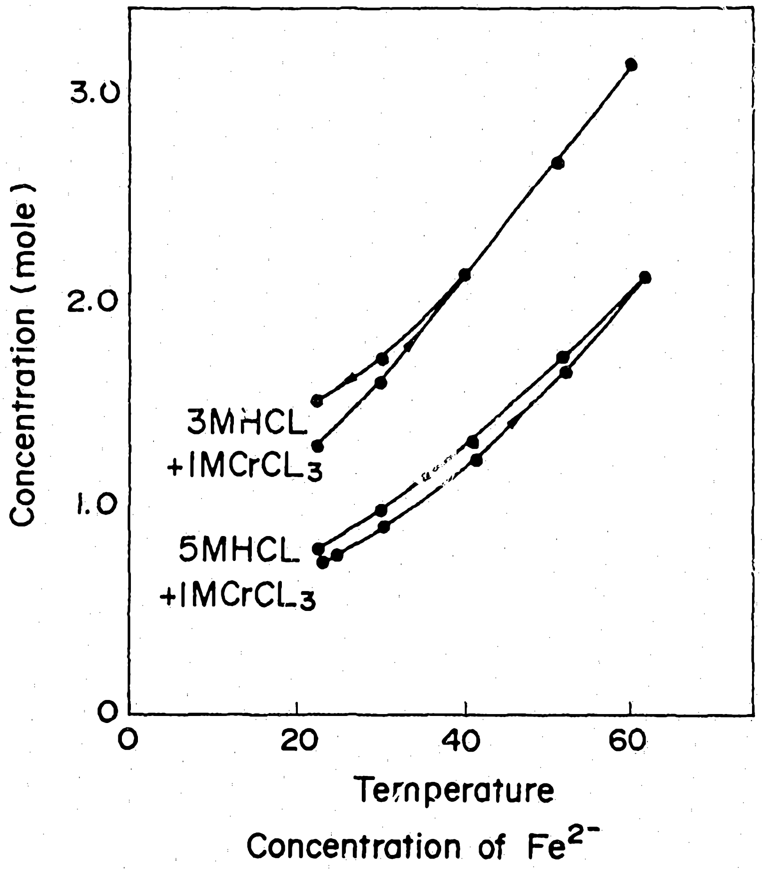
1
2
3
4
H₂SO₄ concentration (M)
concentration
Internal resistance
1 M ●
2 M ▲
3 M ■
4 M ◆
6 M *

Fig. 3


Concentration (mole)
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2.0
1.0
0
3MHCL
+1MCrCL3
5MHCL
+1MCrCL3
0
20
40
60
Ternperature
Concentration of Fe2-