

Process for Recovering Noble Metals from Fluoropolymer-containing ComponentsTechnical Field of the Invention

This disclosure relates to a process of decomposition of noble metal-containing polymeric materials, especially of fluoropolymeric materials and the recovery of said noble metals. In particular, the polymeric materials contemplated are from components involved in hydrogen energy generation and production.

Background to the Invention

Increased demand and legislation to reduce the use of fossil fuels has driven industry to move towards alternative energy sources which produce little to no pollutants, such as hydrogen technology. To effectively use hydrogen as an energy source requires both electrolyzers and fuel cells. Electrolyzers use electrical energy, to split water molecules into hydrogen and oxygen. The hydrogen produced, from either an electrolyser or other sources, can be used in a fuel cell to generate clean energy by utilising the chemical exothermic energy generated when hydrogen reacts with an oxidising agent, typically oxygen gas from air.

Certain fuel cell types and electrolyzers require at least one membrane electrode assembly (MEA). An MEA comprises an assembled stack of polymer electrolyte membranes (PEM) (also referred to as proton exchange membranes), a catalyst, and a flat plate electrode. PEMs typically comprise at least one type of fluoropolymer such as Teflon (RTM). As an example, a platinum based electrode, in which a platinum base is applied to a gas diffusion layer that has a micro-porous layer and Polytetrafluoroethylene (PTFE), has been disclosed in '<https://www.fuelcellstore.com/fuel-cell-components/gas-diffusion-electrode/platinum-electrodes>'.

Polymer Electrolyte Membranes usually consist of a sulphonated fluoropolymer. Teflon (RTM) is added as a binding agent to allow water to escape from or be drawn to the catalyst layer and sometimes replaces Nafion (RTM), also typically used, for that purpose because it is less expensive. Also, coating the gas diffusion layer with Teflon (RTM) prevents the gas diffusion layer from being saturated by liquid water, whilst still letting water vapour through the pores. The catalyst comprises a noble metal, typically platinum.

Current recycling methods for fuel cells and electrolyzers do not efficiently breakdown the fluoropolymers into non-harmful compounds due to their large chain length. Partial breakdown of fluoropolymers can result in the formation of per- and poly-fluorinated alkyl substances (PFAS) which includes non-polymers, such as fluorotelomer alcohols, perfluorocarboxylic acids or perfluorosulfonates. The emission of hydrogen fluoride can also occur during this process. Fluorinated organic chemicals emission into the air and water must be reduced due to the growing number of environmental and health problems that they cause.

10 RU1840855C discloses a method of extracting noble metals from general wastes through reaction with chlorine, introduced through graphite pipes, followed by electrolysis utilising the pipes as an electrode.

In this specification, the term 'noble metal containing component' refers to any compound containing either silver (Ag), gold (Au), platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru), Osmium (Os), or any combination thereof, along with a fluoropolymer. It will be appreciated that the process could also be used in respect of other polymeric materials, and including non-fluorine containing polymers such as polyvinylidene fluoride, Viton (RTM), polyvinyl chloride, High density polyethylene, low density polyethylene, polyether ether ketone, and rubbers.

Summary of the Invention

According to a first independent aspect of the invention there is provided a process comprising selecting components:

- 25 a) a noble metal-containing component, for example those involved in hydrogen energy generation, the component being incorporated into or otherwise bound to a polymer;
- b) an inorganic salt,

30 wherein the components are mixed together and heated in the presence of air to melt the inorganic salt, maintaining the inorganic salt in molten form for a period of 0.5 – 4 hours, cooling to solidify the molten salt, wherein the inorganic salt is a Group II halide.

The noble metal-containing component is typically recovered from a fuel cell and/or an electrolyser. For example, the component is obtained from the fuel cells and/or

35

electrolysers catalyst coated membranes (CCM) and/or a membrane electrode assemblies (MEAs) and/or a catalyst paste and/or production scraps.

- The process includes the use of a preferably eutectic molten salt in the form of an inorganic halide as an electrolyte mixture to decompose fluoropolymer constituents and refine the noble metals. Preferably the Group II halide is a calcium chloride. Additionally or alternatively, the inorganic salt includes a Group I alkali metal halide, preferably the halide is a chloride ion. In a preferred embodiment, the inorganic additive used is either sodium chloride (NaCl) and/or potassium chloride (KCl). Advantageously, the resulting electrolyte, when molten, will decompose any fluorocarbon polymer, such as Teflon (RTM) or Nafion (RTM), to fluorine anions (F^-) and/or carbon monoxide (CO) and/or carbon dioxide (CO_2). A further advantage of using the electrolyte mixture in this process is the capacity to produce an ionic current over a wide temperature range. The ionic current dissolves and transports anions such as, but not exclusively, oxide anions (O^{2-}) and/or sulphide anions (S^{2-}) and/or fluoride anions (F^-) and/or chloride anions (Cl^-), which are formed during the thermal decomposition of fluoropolymers. A further advantage for use of the electrolyte in the process is the reduced solubility exhibited by the noble metals allowing for greater extraction potential.
- In a further dependent aspect, the components are heated within a range of $700^{\circ}C$ – $1100^{\circ}C$. Preferably, the components are heated within $700^{\circ}C$ - $1000^{\circ}C$. For example, the components are heated, in the presence of air, to a temperature of $900^{\circ}C$, a much lower temperature than previously disclosed which advantageously reduces the energy demands required to melt the components.
- In a further dependent aspect, the noble metals are extracted from the resulting solidified inorganic salt mixture containing noble metals. For example, the solidified salt is converted into a friable salt mixture which can be milled into a fine powder containing the noble metal. For example, such extraction methods may include dissolution of the noble metals via *aqua regia* followed by solid liquid separation techniques. A further alternative example includes leaching of the noble metals from the salt mixture via the addition of a concentrated acid. Further processing via solid-liquid separation is then employed to concentrate the noble metals.
- In a further dependent aspect, the inorganic salt mixture containing noble metal or metals is heated till molten, with the noble metal or metals subsequently being collected via a suitable collector from the molten salt bath.

In an independent aspect, a resulting inorganic salt mixture containing noble metals is produced from the disclosed process and is suitable to undergo further refinement and extraction treatments. Methods to concentrate the noble metals and extract from the salt mixture include, but are not exclusive to:

- 5 - Dissolution of the noble metals via *aqua regia*, followed by a solid liquid separation method to remove the insoluble fluoride salt. Subsequent cementation of pregnant solution to prepare a cementation residue containing the noble metals
 - 10 - Hydrochloric acid leaching of salt mixture via acidic pH levels. The fluoride-containing salt remains insoluble along with the noble metals, a solid-liquid separation is then employed to yield a concentrate of noble metals and calcium fluoride
 - Collection of noble metals with a suitable collector from the molten salt bath.
- 15 In an independent aspect, the heat treatment process is conducted in one step in a batch operation. The component parts, for example CCM/MEA, may be used whole or in a shredded / cut form. The pieces are assembled in a tray-like device in layers with the salt mixture intercalated. The tray-like device may be manufactured from a grade of steel. The whole tray is heated using electrical or gas fired control to meet the
- 20 temperature.

In an independent aspect, the heat treatment process is conducted in a continuous process. A molten salt bath is created of particular composition by applying electrical or gas fired heat control to reactor manufactured of a grade of steel or superalloy which may

25 have a refractory lining. The CCM or MEA parts may be added whole or pre-shredded to the bath using a basket to contain the parts until they are fully digested. The bath composition is sampled periodically where additional components may be added.

Detailed Description of the Invention

30 The description comprises example methods for the recovery of metals from noble metal-containing polymeric materials. The method involves reclaiming inherently valuable precious metals which are attached or incorporated either within or on the surface of the noble metal-containing polymeric materials. The process involves engaging the polymeric material with a molten ionic salt which on cooling produces a friable solid material which

35 is capable of undergoing further processing to recover the precious metals whilst safely

handling other elements such as fluorine. The friable material, for example calcium fluoride, can subsequently utilised in the manufacture of fluorine-containing materials such as fluoropolymers, such as for membranes, thus achieving circularity in the process.

- 5 The following examples refer to the noble metal-containing polymeric materials originating from components involved in hydrogen energy generation and production, however, it will be appreciated that alternative origins for the noble metal-containing polymeric materials could be applied.
- 10 The features and aspects of the embodiment are described in detail below with reference to examples.

Example 1

- 15 This example describes the recovery of platinum on carbon from a fluoropolymer membranes using the disclosed process.

A composition was prepared by thoroughly mixing together the following components:-

5-layer fluorocarbon polymer-containing membrane electrode assembly (MEA) containing 5% platinum by weight.	10 g
Calcium chloride	75 g
Calcium acetate	25g

- 20 The MEA contains 0.45mg Pt cm^{-2} in the form of platinum on carbon black which equates to roughly 5% platinum by weight, 0.5 g (=2.5 mmoles Pt). The calcium chloride salt has the general formula CaCl_2 and is used in the dried, reagent-grade form

- 25 The composition was heated in a furnace at 900°C in an aluminum oxide crucible and held at this temperature for four hours. At this temperature the electrolyte is molten and capable of decomposing fluoropolymers to F^- , CO , CO_2 , as well as dissolving and transporting anions that are formed during the thermal degradation of the fluoropolymers. The CO and CO_2 typically are vented to atmosphere. The molten salt was then solidified by cooling, converting the noble metal-containing material into a friable solid salt mixture which was milled to a fine powder. Analysis using Inductively Coupled Plasma Optical

Emission spectroscopy (ICP-OES) showed >99% recovery of platinum from the MEA, as a solid salt mixture.

Although exemplified here for an iridium/platinum containing material, the process can also be used for ruthenium-containing materials or materials containing mixtures of these elements. Moreover, the method is also suitable for materials containing silver, gold, palladium, rhodium, and osmium or mixtures thereof, including with platinum, iridium and ruthenium.

10 Example 2

This example describes the recovery of the noble metals, iridium and platinum, from a fluoropolymer membrane containing iridium (IV) oxide and platinum using the disclosed process.

A composition was prepared by thoroughly mixing together the following components:-

Electrolyser scrap containing 3% iridium and 1% platinum by weight.	1 g
Calcium chloride	7.5 g
Calcium acetate	2.5g

The CaCl_2 is the preferred salt for this process, since it has a lower melting point than most other group I and II calcium salts. To enable complete fluoride recovery a basic salt must be added such as calcium acetate.

The composition was heated in a furnace to 750°C in an aluminum oxide crucible for 1 hour. The molten salt composition was solidified by cooling, leached with water and hydrochloric acid until acidic in pH, dried, milled to a fine powder, and analyzed by ICP-OES to show >99.6% of the iridium and >99.4% of the platinum were recovered from the scrap electrolyser. The acid leach ensures the Pt and Ir concentration in the final solids are at higher concentrations than the starting material, and provides a solid which has minimal deliquescent properties making it ideal for milling.

Although exemplified here for an iridium/platinum containing material, the process can also be used for ruthenium-containing materials or materials containing mixtures of these

elements. Moreover, the method is also suitable for materials containing silver, gold, palladium, rhodium, and osmium or mixtures thereof, including with platinum, iridium and ruthenium.

5 Example 3

This example describes an alternative process for extraction of platinum from the solidified salt mix generated in Example 1.

An extraction composition was prepared by mixing together the following ingredients:-

Milled salt mixture containing 0.5 wt. % platinum extracted via Example 1 method.	20 g
Water	100 mL
Concentrated hydrochloric acid 37%	75 mL
Concentrated nitric acid 68%	25 mL

- 10 The water, concentrated hydrochloric acid and concentrated nitric acid is mixed to a preferred volume ratio of 4:3:1. The undissolved calcium fluoride was separated by a suitable solid liquid separation method of which would be known to a person skilled in the art.

15 Example 4

This example describes an alternative process for extraction of platinum from the solidified salt mix generated in Example 1.

An extraction composition was prepared by mixing together the following ingredients:-

Milled salt mixture containing 0.5 wt. % platinum extracted via Example 1 method.	20 g
Water	200 mL

- 20 The extraction solution was adjusted to pH 4 via the addition of concentrated 37% hydrochloric acid. The pH shift causes the calcium salts other than fluoride to solubilize whereas the platinum and calcium fluoride remain insoluble. Efficiency of platinum extraction is >99% by virtue of the insolubility of metallic platinum in the absence of an oxidizing agent.

Example 5

This example describes an alternative process for extraction of platinum from the solidified salt mix generated in Example 1.

An extraction composition was prepared by mixing together the following ingredients:-

Milled salt mixture containing 0.5 wt. % platinum extracted via Example 1 method.	20 g
--	------

Tin powder (200 mesh; 74 µm)	10 g
------------------------------	------

5

The extraction composition was then heated at 1100 °C for 1 hour 30 minutes in a ceramic crucible with an air supply. The resulting compound was cooled and mixed with concentrated hydrochloric acid 200 mL which acts as a solvent and lixiviant for metallic tin. The solute leaches into the hydrochloric acid, leaving the undissolved platinum which
10 can be recovered by solid liquid separation methods. The recovery of platinum was 64% by ICP-OES analysis of the black undissolved residue. The remaining platinum, 36% was found in the slag phase from the smelting process, with no platinum being detected in the hydrochloric acid leachate.

15 In relation to the methods disclosed in Examples 1 and 2, the reaction time can be within the preferred range of 0.5 – 4 hours. A shorter reaction time can be advantageous as the metals being recovered are then less likely to form soluble products in the subsequent leaching steps.

20 The temperatures to which components are heated in Examples 1 and 2 are preferable within the range of 700°C – 1100°C, and further preferably 700°C – 1000°C. A lower temperature as the metals being recovered are then less likely to form soluble products in the subsequent leaching steps.

25 The CCM/MEA parts may be used whole or in a shredded / cut form. The pieces can be assembled in a tray-like device in layers with the salt mixture intercalated. The tray-like device may be manufactured from a grade of steel. The whole tray is heated using electrical or gas fired control to meet the temperature.

Although the disclosed subject matter has been described using specific terminology relating to apparatus features and/or method features, it is to be understood that the claimed subject matter is not necessarily limited to the examples disclosed. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all
5 such modifications and equivalent structures and functions. The advantages disclosed may relate to several of the examples that are disclosed.

Claims

1. A process comprising selecting components:
 - a) a noble metal-containing component for example those involved in hydrogen energy generation, the component being incorporated into or otherwise bound to a fluoropolymer;
 - b) an inorganic salt,wherein the components are mixed together and heated in the presence of air to melt the inorganic salt, maintaining the inorganic salt in molten form for a period of 0.5 – 4 hours, cooling to solidify the molten salt, wherein the inorganic salt is a Group II halide.
2. A process according to Claim 1, wherein the molten inorganic salt is a eutectic molten salt.
3. A process according to Claim 1 or Claim 2, wherein the inorganic salt is calcium chloride.
4. A process according to Claim 3, wherein the inorganic salt also includes a Group I alkali metal halide.
5. A process according to Claim 4, wherein the halide is chloride.
6. A process according to Claim 4 or Claim 5, wherein the alkali metal halide is selected from sodium chloride or potassium chloride.
7. A process according to any preceding claim, wherein the components are heated within a range of 700°C – 1100°C.
8. A process according to Claim 7, wherein the components are heated within a range of 700°C – 1000°C.
9. A process according to any preceding claim, wherein in a further step the noble metals are extracted from the resulting solidified inorganic salt mixture containing noble metals.
10. A process according to Claim 9, wherein the further step comprises converting the solidified salt into a friable salt mixture and milling said solid into a powder.
11. A process according to Claim 10 or Claim 10, wherein the solid is contacted with *aqua regia* to dissolve the metals followed by applying solid liquid separation techniques.
12. A process according to Claim 9 or Claim 10, wherein the solid is contacted with concentrated hydrochloric acid to dissolve the metals followed by applying solid liquid separation techniques

13. A process according to any preceding claim, wherein the component is in a shredded / cut form.
14. A process according to Claim 13, wherein the noble metal-containing component is assembled in a tray-like device in layers with the salt mixture intercalated.
- 5 15. A process according to Claim 13, wherein the tray-like device is formed of steel.