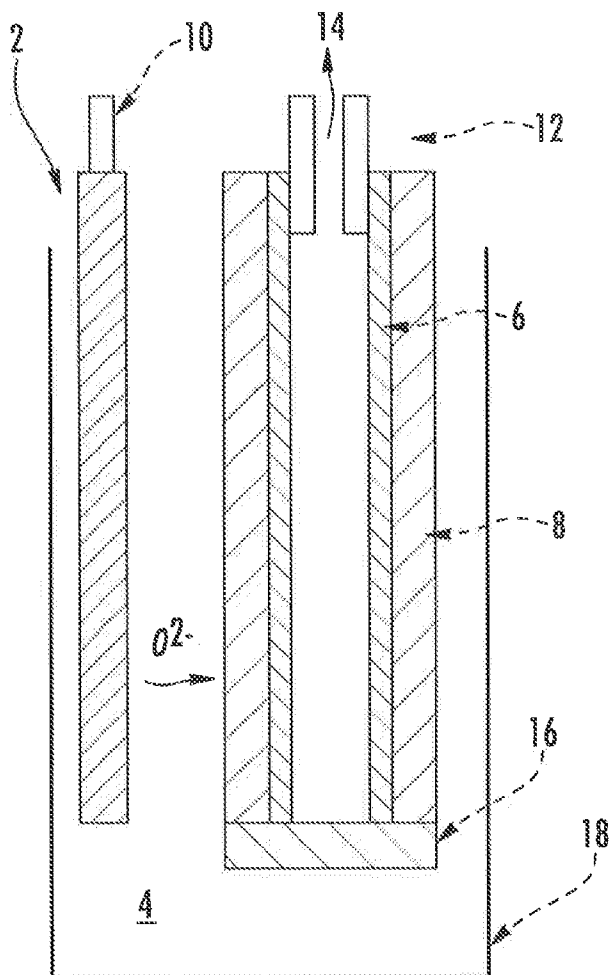




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(19) **United States**(12) **Patent Application Publication**  
**Brinkman et al.**(10) **Pub. No.: US 2016/0032473 A1**(43) **Pub. Date: Feb. 4, 2016**(54) **ELECTROCHEMICAL CELL FOR  
RECOVERY OF METALS FROM SOLID  
METAL OXIDES**(52) **U.S. Cl.**  
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*C25C 7/02* (2013.01)(71) Applicant: **Savannah River Nuclear Solutions,  
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(US); Joshua R. Gray, Aiken, SC (US)**(73) Assignee: **Savannah River Nuclear Solutions,  
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An electrochemical cell and methods of using the electrochemical cell are described that can be utilized for the recovery of metals from metal oxides. The cell includes a first electrode that includes a solid metal oxide, an electrolyte including an oxygen ion conductor, and a second electrode space apart from the electrolyte by an oxygen ion conducting membrane. Upon reduction of the metal oxide, solid metal is formed that replaces the metal oxide of the electrode and provides for simplified recovery of the metal from the metal oxide. The membrane protects the second electrode from corrosion and degradation from the electrolyte, increasing the life of the cell.



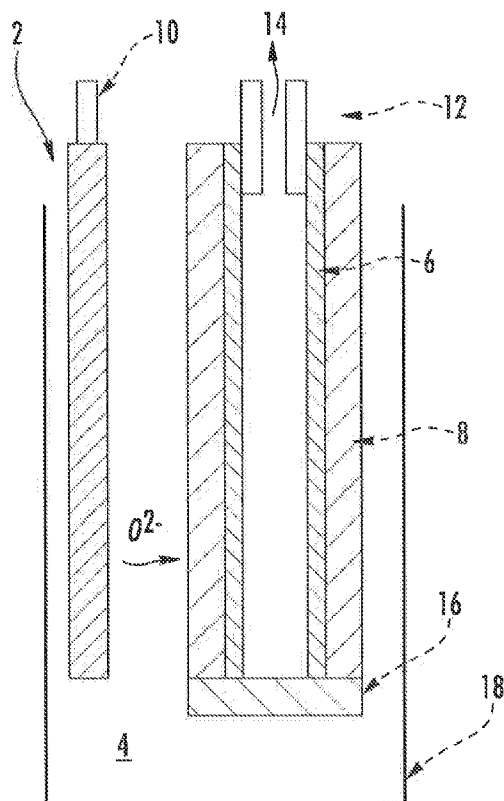


FIG. 1

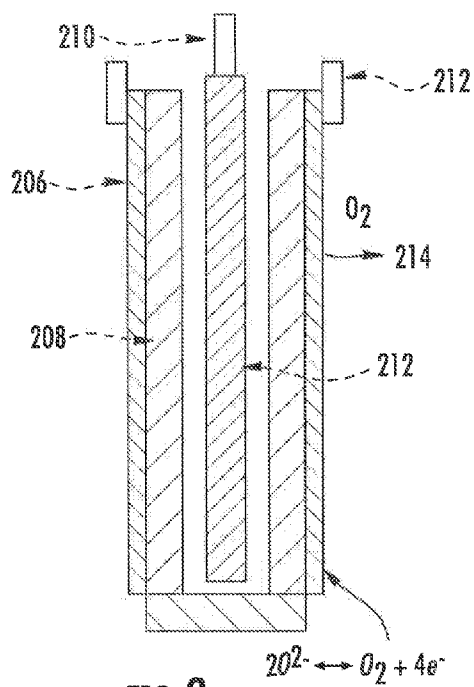
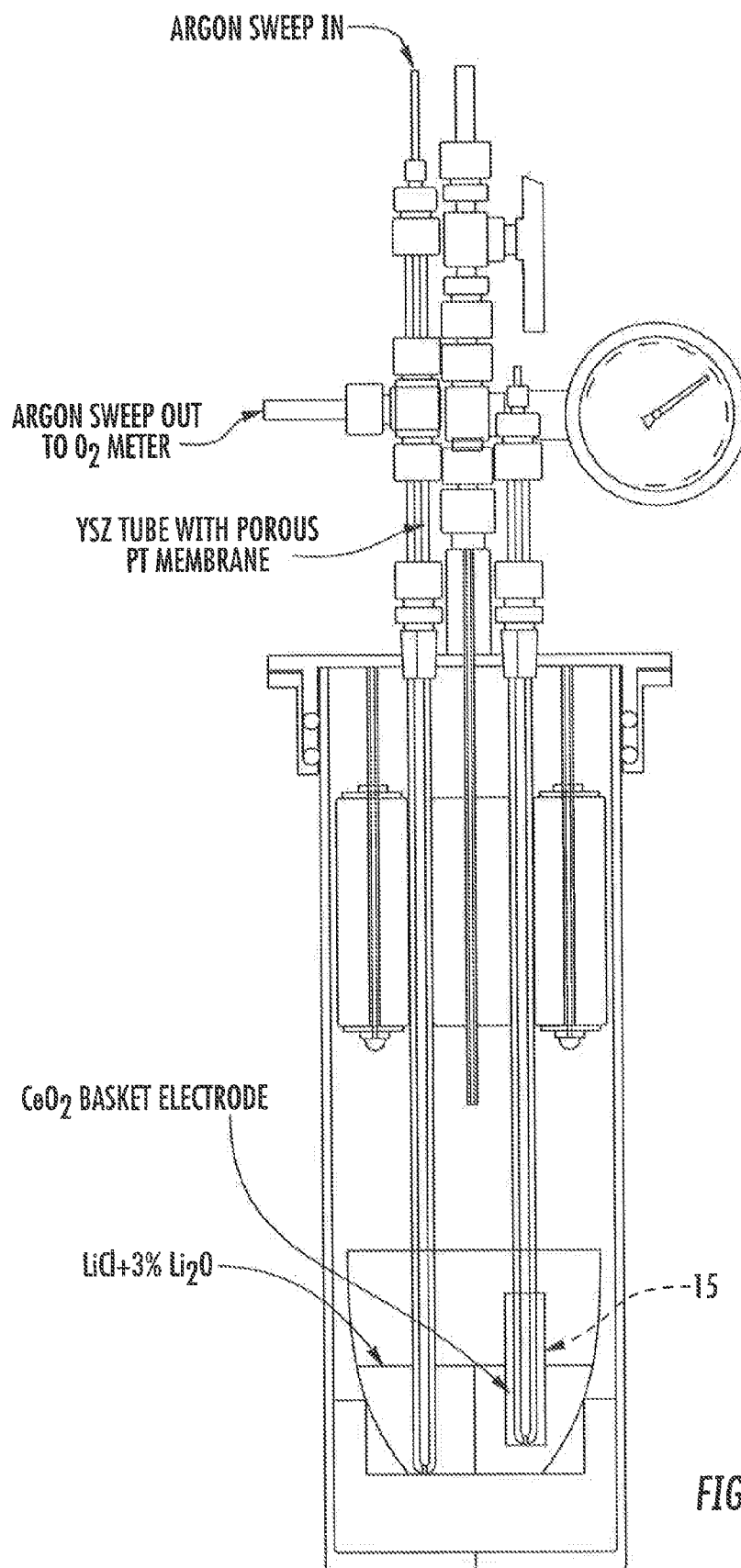


FIG. 2



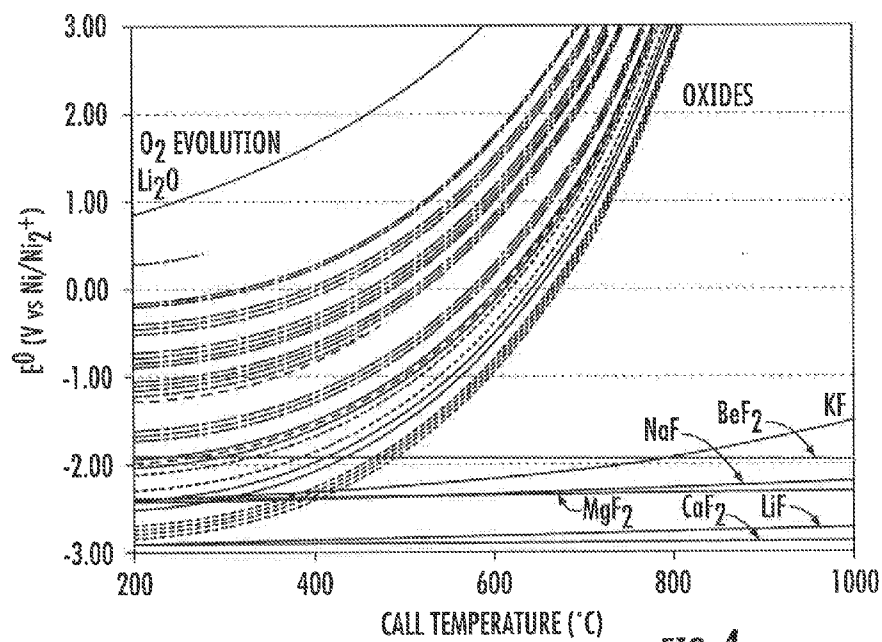


FIG. 4

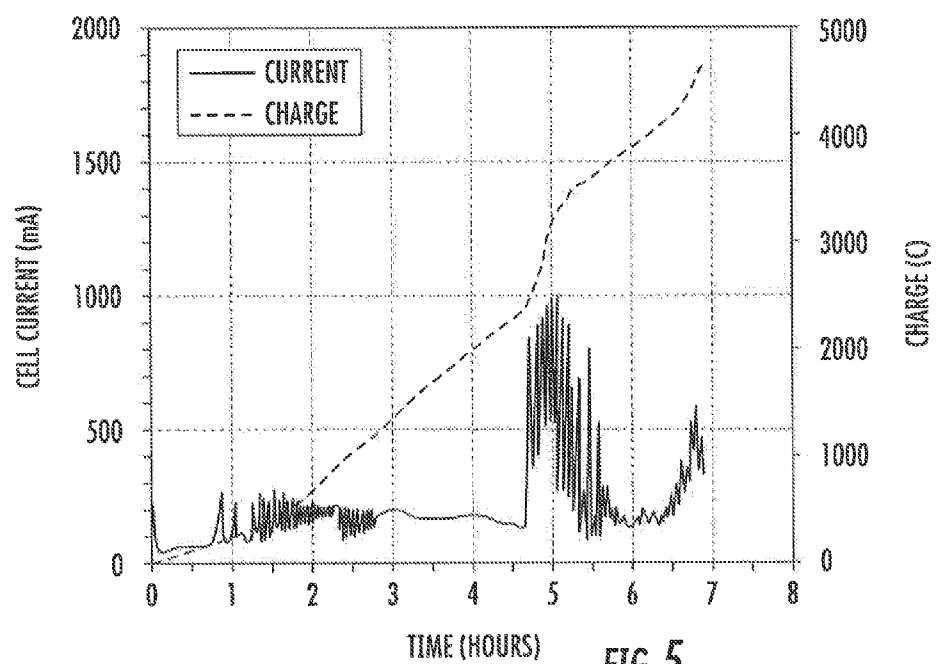


FIG. 5

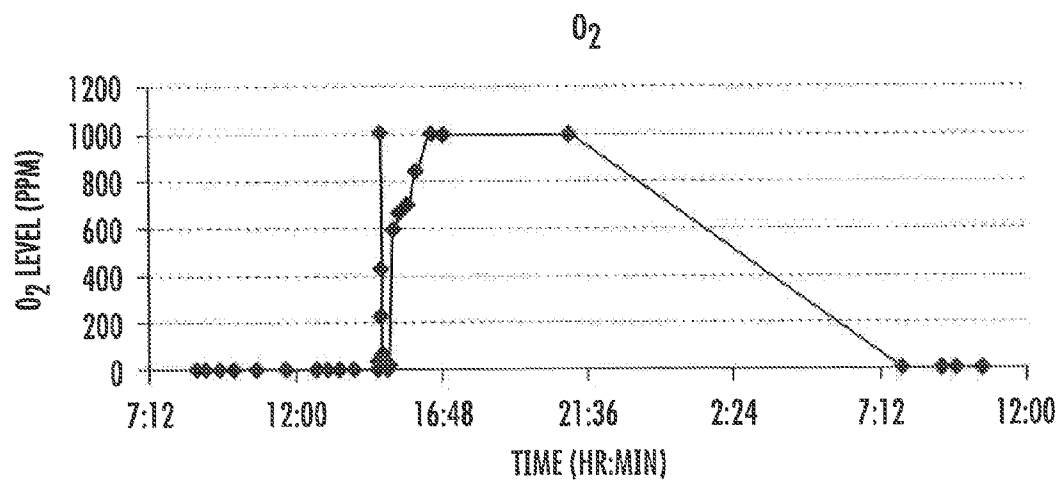


FIG. 6

**ELECTROCHEMICAL CELL FOR  
RECOVERY OF METALS FROM SOLID  
METAL OXIDES**

STATEMENT AS TO RIGHTS TO INVENTIONS  
MADE UNDER FEDERALLY SPONSORED  
RESEARCH

[0001] This invention was made with Government support under Contract No. DE-AC09-08SR22470 awarded by the United States Department of Energy. The Government has certain rights in the invention.

BACKGROUND

[0002] Electrolytic processes have been used to recover high purity metals (e.g., uranium) from the mixture of elements in used nuclear fuel, also known as spent nuclear fuel, as well as from mined ores containing desirable metals. Generally, these processes are carried out in electrochemical cells in which an oxide of the metal to be recovered (e.g., uranium oxide) is dissolved in a molten salt electrolyte. The cells also include two electrodes that can be submerged in the molten salt electrolyte. The first electrode can include an inert electron-conducting material such as steel or other suitable metal and the second electrode can encourage oxidation of oxygen ions. Upon establishment of a suitable voltage potential across the cell, the dissolved metal oxide dissociates into the ionic species. The molten salt electrolyte is an ionic conductor that allows the ionic species to separate, with the metal ions driven to and being deposited at the first electrode and the oxygen ions driven to the second electrode where oxidation occurs and molecular oxygen, carbon monoxide, carbon dioxide, or the like is generated.

[0003] Oxygen ion conducting membranes, such as yttria-stabilized zirconia membranes, have also been incorporated in these types of electrochemical cells. Such membranes can improve separation of the ionic species within the cells and help to prevent corrosion of the electrodes.

[0004] Unfortunately, problems still exist with electrochemical cells for metal recovery and purification. For instance, systems in which the metal oxide feed is dissolved in the electrolyte require substantial amounts of the electrolyte due to low solubility. In addition, the metallic ion deposition on the electrode decreases surface area and limits current density of the system. Additionally, many inert anode materials including platinum can be consumed with time through the formation of complexes with oxygen and salt species.

[0005] What are needed in the art are methods and systems that can selectively recover targeted metals from oxides and in one embodiment can recover uranium from uranium oxide in spent nuclear fuel.

SUMMARY

[0006] Aspects and advantages of the invention will be set forth in part in the following description, or may be obvious from the description, or may be learned through practice of the invention.

[0007] In one embodiment disclosed herein is an electrochemical cell that includes a first electrode and a second electrode. More specifically, the first electrode includes a solid metal oxide and a first current collector and the second electrode includes a material that encourages the oxidation of oxygen ion and a second current collector. The electrochemi-

cal cell also includes an electrolyte that in turn includes an alkali metal or alkaline earth metal salt or a eutectic or mixture thereof that is molten at the operating temperature of the cell. An oxygen ion conducting compound is mixed with the electrolyte. In addition, the electrochemical cell includes an oxygen ion conducting membrane that separates the electrolyte from the second electrode.

[0008] Also disclosed is a method for recovering a metal from a metal oxide. The method can include locating the first electrode in the electrochemical cell and applying a voltage potential across the first and second electrodes. The voltage potential is greater than the dissociation potential of the metal oxide and thus drives reaction of the metal oxide to form oxygen ions and a solid metal in the place of the solid metal oxide of the first electrode. The oxygen ions are conducted across the electrolyte via the oxygen ion conductor and across the oxygen ion conducting membrane to the second electrode. The oxygen ions are oxidized at the second electrode to form a molecular oxygen species (e.g., molecular oxygen, carbon dioxide, etc.).

[0009] In one particular embodiment, the first electrode includes a solid uranium oxide and a current collector and the method can be used to purify uranium from spent nuclear fuel.

[0010] These and other features, aspects and advantages of the present disclosure will become better understood with reference to the following description and appended claims.

BRIEF DESCRIPTION OF THE FIGURES

[0011] A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth in the specification, which makes reference to the appended figure, in which:

[0012] FIG. 1 schematically illustrates one embodiment of an electrochemical cell as described herein.

[0013] FIG. 2 schematically illustrates another embodiment of an electrochemical cell as described herein.

[0014] FIG. 3 illustrates an electrochemical cell utilized in the Example section described herein.

[0015] FIG. 4 graphically illustrates the equilibrium potential of the cell with cell temperature for several different molten salt electrolytes and for lithium oxide.

[0016] FIG. 5 illustrates the change in cell current and charge with time during cell operation.

[0017] FIG. 6 illustrates the oxygen generated at the second electrode with time during cell operation.

DETAILED DESCRIPTION

[0018] It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present disclosure. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment can be used with another embodiment to yield a still further embodiment. Thus, it is intended that the present invention covers such modifications and variations as come within the scope of the appended claims and their equivalents.

[0019] The present disclosure is generally directed to an electrochemical cell and methods of using the electrochemical cell. More specifically, the electrochemical cell can be utilized for the recovery of metals from metal oxides. Without wishing to be bound by any particular theory, it is understood that as the reduction reactions begin at the metal oxide-containing electrode, conductive reaction products are formed and the effective contact area between the conductive elements of the electrode and the oxides of the electrode will increase. This can increase the reaction rate (which can be demonstrated by an increase in current in the cell) and drive the complete reduction of the solid metal oxide. For instance, when considering a metal oxide such as  $\text{CeO}_2$ , as the reduction reaction takes place at the electrode, metallic (and conductive) cerium will be formed. As the metallic cerium is formed where the cerium oxide contacts the current collector, the conductive phase of the electrode will grow, which can increase the current across the cell and increase the reaction rate for the metal formation.

[0020] The reaction rates of the cell can increase quickly leading to reduction of the metal oxide in relatively short order when processing metal oxides that form Magneli phases, which are electrically conductive sub-stoichiometric phases that can form prior to complete reduction to the metal and dissociation of the oxygen ion. Such phases are known for certain metal oxides including titanium dioxide and uranium dioxide, and may exist for others. Upon initiation of the reduction process, the formation of the conductive sub-stoichiometric phases (e.g.,  $\text{Ti}_4\text{O}_7$ ,  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$ , etc.) will encourage increase in conduction and increase in conductive surface area throughout the electrode and thus further reduction to the pure metal.

[0021] One embodiment of an electrochemical cell is illustrated in FIG. 1. In general, the electrochemical cell can include a first electrode 2, an electrolyte 4 that has an oxygen ion conducting compound mixed with the electrolyte, an oxygen ion conducting membrane 8, and a second electrode 6. The first and second electrodes 2, 6 are in electrical communication with one another via a first current collector 10 of the first electrode 2 and a second current collector 12 of the second electrode 6 that are electrically connected to one another in conjunction with a device or system that can establish a voltage potential across the first electrode 2 and the second electrode 6. In conjunction with the current collector 10 of the first electrode, the first electrode also includes a solid oxide of the metal to be recovered.

[0022] Upon establishment of a voltage potential across the cell that is greater than the dissociation potential of the metal oxide of the first electrode 2, dissociation reactions will begin that form oxygen ions and the reduction product(s) of the dissociation and reduction at the first electrode. As previously mentioned, the reduction products can initially include both the reduced metal and Magneli phases, depending upon the particular metal oxide of the first electrode. The voltage potential can drive the oxygen ions across the electrolyte 4 via the oxygen ion carrying compound that is combined with the electrolyte 4 in a mixture. The oxygen ions can then be conducted across the membrane 8 to the second electrode 6, where they are oxidized and can exit the cell, as at 14. Thus, as the metal oxide dissociates and the oxygen ion is driven away from the first electrode and toward the second electrode, the metal ions are reduced to form the metal, which replaces the metal oxide of the first electrode.

[0023] Following dissociation of the metal oxide to leave the purified metal in place of the original metal oxide of the first electrode 2, the electrode 2 can be simply removed from the electrochemical cell and replaced with a new electrode that includes metal oxide. Thus, use of the cell can provide the purified metal in an easily retrievable form and allow for faster and more economical recovery of purified metals from metal oxides.

[0024] The electrochemical cells and methods utilizing the cells can be particularly useful for recovery of uranium from spent nuclear fuel that contains uranium oxide. It should be understood that the electrochemical cell is not limited to this use, however, and may advantageously be utilized to recover purified metals of any type from the oxide form of the metal. For instance, the electrochemical cell may be useful in recovery of metals from mining operations or in recycling operations, for instance in recovery of rare earth metals from ores.

[0025] The electrode 2 can include the metal oxide in any suitable form. For instance, in one embodiment the metal oxide can be preprocessed according to standard methodology to increase the surface area. By way of example, the metal oxide can be chopped or ground prior to location in the electrochemical cell to form metal oxide particles that can have a cross sectional dimension of about 2 millimeters or less, for instance about 1 millimeter or less in some embodiments, about 500 nanometers or less in some embodiments, or about 100 nanometers or less in some embodiments. In such an embodiment, it can be beneficial to contain the particles of metal oxide of the electrode 2 within a container, which can be, for example, a basket or other suitable container.

[0026] The used metal oxide can be preprocessed according to other processing techniques as are known in the art. For instance used nuclear fuel including uranium dioxide can be subjected to high temperature treatments including voloxidation that can be utilized to capture tritium, iodine, technetium, etc. The pre-processing steps may remove all or part of specific fission products. It should be understood, however, that this disclosure applies to any metal oxide composition that can result from any combination of pre-processing steps.

[0027] When utilized, an electrode container (15, FIG. 3) can be formed of any suitable material that is resistant to the components of the cell (e.g., the molten salts of the electrolyte) and that can provide contact between the electrolyte and the metal oxide of the first electrode held in the container. For instance, the container can be a porous container formed of a corrosion resistant material including carbon compounds such as graphite or glassy carbon, ceramics such as silicon carbide or boron nitride, a corrosion resistant metal alloy, or composite material including carbon and ceramics, or a perfluorinated plastic material, such as a polyfluoroethylene, provided the material can withstand the operating temperatures of the cell. In one embodiment, a container can be formed of a glassy carbon material. In general, any metal of the container can be insulated from the metal oxide held within the container, for instance by inclusion of an insulative covering on at least that portion of a metal or metal alloy of the container that would otherwise contact the metal oxide of the first electrode.

[0028] As previously stated, the metal oxide of the first electrode 2 can be provided in a high surface area form such as chopped or ground materials. This is not a requirement of the electrochemical cell, however, and the metal oxide may be in the form of a single or multiple solid pieces that can include

porosity or not, as desired. For instance, the metal oxide of the first electrode **2** can include a plurality of pores that extend across all or a portion of a single solid metal oxide piece. For example, a porous metal oxide component of the first electrode **2** can have a void fraction of from about 5% to about 90%, from about 10% to about 80%, or from about 20% to about 70%.

**[0029]** The oxygen ion formed upon dissociation of the metal oxide can diffuse out of the first electrode **2** to the electrolyte **4**. Beneficially, at the operating temperatures of the cell (about 200° C. or greater, about 400° C. or greater, or about 600° C. or greater, in some embodiments), oxide ion can diffuse through metal that may have already formed in the first electrode **2**. This allows for the metal oxide conversion to be carried out throughout the depth of the solid oxide material of the first electrode **2** and provides in one embodiment for complete conversion of the metal oxide to the desired metal.

**[0030]** The electrode **2** can include current collector **10** that can be capable of use at the expected operating temperatures of the electrochemical cell. Examples of electrically conductive materials from which the current collector **10** can be formed include, without limitation, metallic materials based on nickel, tungsten, molybdenum, and cobalt as well as carbon based materials such as glassy carbon and graphite. Alloys including refractory metals such as niobium, molybdenum, tantalum, tungsten, and rhenium as well as conductive ceramics and composite materials can also be utilized in forming the current collector **10**. For example, stainless steel may be utilized as a current collector in some embodiments.

**[0031]** It may be useful in some embodiments to provide the current collector **10** in an arrangement with the metal oxide so as to provide for a high contact area between the two, as this can increase the starting reaction rate of the dissociation and reduction reactions. For instance, the current collector **10** can be in the form of a high surface area plate or leaf that is submerged within the metal oxide to allow for maximum possible contact area between the two. In another embodiment, the metal oxide can be in the form of particles and the container used to hold the particles can also function as a current collector, which can provide a high contact area between the current collector and the metal oxide of the first electrode **2**.

**[0032]** The electrolyte **4** includes one or more salts that can be held in the form of a molten salt electrolyte bath during operation of the cell **10**. As is known in the art, the salts can include any alkali metal or alkaline earth metal halide salt, or eutectics or mixtures thereof. For example, the electrolyte can include one or more chloride salts of sodium, potassium, lithium, magnesium, calcium, aluminum, one or more fluoride salts of sodium, potassium, lithium, magnesium, calcium, aluminum, cryolite ( $\text{Na}_3\text{AlF}_6$ ), mixtures thereof, and so forth.

**[0033]** In conjunction with the electrolyte **4**, the electrochemical cell can also include an oxygen ion conducting compound. The ion conducting compound can be an oxygen ion conducting oxide that is an alkali metal or alkali earth metal oxide such as an oxide of lithium, calcium, aluminum, magnesium, zinc, silicon, titanium, lead, or mixtures thereof. In one embodiment, the ion conducting compound can include an oxide of the metal to be recovered.

**[0034]** The electrochemical cell also includes an oxygen ion conducting membrane **8** that separates the electrolyte **4** from the second cathode **6**. The oxygen ion conducting membrane **8** can have a molecular framework structure that per-

mits the oxide ions to move from the electrolyte **4** to the second cathode **6**, without exposing the second cathode **6** to the molten salts of the electrolyte **4**. The oxygen ion conducting membrane **8** can include a solid electrolyte composition formed between oxides containing divalent and/or trivalent cations such as alkaline earth oxides, e.g., calcium oxide, or rare earth oxides, e.g., scandium oxide, yttrium oxide, lanthanum oxide, etc., and oxides containing tetravalent cations such as zirconia, hafnia, thorium and ceria. For instance, the oxygen ion conducting phases of the membrane **8** can be a mixed metal oxide having a fluorite structure, for instance a doped fluorite compound. The fluorite crystal structure can provide large amounts of oxygen vacancy when substituted with the aliovalent oxides. For instance, one oxygen ion vacancy can occur for each divalent or each two trivalent cations that are substituted for a tetravalent ion in the lattice. Accordingly, the membrane can exhibit high oxygen mobility and oxygen ion conduction.

**[0035]** In one embodiment the oxygen ion conducting membrane **8** can include zirconia ( $\text{ZrO}_2$ ) or hafnia ( $\text{HfO}_2$ ) stabilized in cubic form by a divalent or trivalent metal oxide dopant such as MgO, NiO, SrO, CaO, NiO,  $\text{Y}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$ . In one embodiment the oxygen ion conducting membrane **8** can include zirconia stabilized by addition of yttria ( $\text{Y}_2\text{O}_3$ ). In another embodiment, the oxygen ion conducting membrane **8** may comprise predominately hafnia or ceria ( $\text{CeO}_2$ ) doped with one or more divalent or trivalent metal oxides. Additional examples of materials for the oxygen ion conducting membrane **8** include strontium- and magnesium-doped lanthanum gallate (LSGM). Many other oxides are known which have demonstrated oxygen ion-conducting ability, which could be used as the oxygen ion conducting membrane **8**.

**[0036]** Other additives that may be found in the oxygen ion conducting membrane **8** can include, without limitation,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . These oxides may provide other benefits, such as mixed conduction and lower overvoltage.

**[0037]** The oxygen ion conducting membrane **8** may generally be provided as a layer or sheet electrically connected to the second electrode **6** and forming a barrier between the second electrode **6** and the electrolyte **4**, as shown in FIG. 1. By way of example, the oxygen ion conducting membrane **8** can have a thickness of about 0.5 millimeters or less, or about 0.2 millimeters or less in some embodiments. The solid oxide electrolyte membrane can be in any shape, however, and is not limited to a layer or sheet. In the embodiment illustrated in FIG. 1 the oxygen ion conducting membrane **8** is in a tubular shape, with one end of the tube being closed with a plug **16** formed of a suitable material that can withstand the operating temperatures of the cell, for instance a metallic or polymeric plug **16**. Another suitable shape illustrated in FIG. 2 and discussed further herein is in the form a container **208** that can hold the electrolyte **204**.

**[0038]** Referring again to FIG. 1, the electrochemical cell also includes a second electrode that includes a material to encourage oxidation of the oxygen ion to produce molecular oxygen. Suitable oxygen-producing materials possess high electronic conductivity (for example about 10 S/cm or greater) and charge transfer/surface exchange kinetics (for example about  $10^{-7}$  cm/s or greater), are stable in the oxidizing and temperature environment of the second electrode (generally about 1000° C. or greater) and are chemically, mechanically and structurally compatible with the oxygen ion conducting membrane **8**.



**[0039]** Exemplary oxygen-producing materials of the second electrode include, without limitation, a noble metal (e.g., platinum), silver alloys (Silver-Copper, Silver-Tin etc.), cermets, electronic oxides and composites thereof with stabilized zirconia. A cermet can be for example a composite of an oxygen stable noble metal such as iridium or platinum and a stabilized zirconia. The noble metal can be capable of withstanding the operating temperatures of the cell without melting. Stabilized zirconia may be a rare earth element- or alkaline earth-stabilized zirconia, such as zirconia stabilized with yttria, calcium oxide, scandium oxide and the like as discussed above. Other cermets as are known in the art may be utilized. For instance, a cermet including a sintered combination of iron and nickel oxides with copper and/or silver may be utilized.

**[0040]** In another embodiment, the second electrode can include an oxygen stable electronic oxide such as strontium-doped lanthanum manganite ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM)). Other stable electronic oxides as may be utilized include A-site deficient acceptor-doped lanthanum ferrite and lanthanum cobaltite, e.g.,  $\text{La}_{1-x}\text{A}_x\text{FeO}_3$  and/or  $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ . The oxygen producing materials may include one or more dopants from the group consisting of Ca, Ce, Pr, Nd, and Gd in the La site and from the group consisting of Ni, Cr, Mg, Al, and Mn in the Fe or Co site; Fe may also be used as a dopant in the cobalt site.

**[0041]** Dopant materials and amounts for electronic oxides such as lanthanum ferrite and the lanthanum cobaltite may be selected to decrease the thermal expansion of the ceramic and to provide a closer thermal match to the oxygen ion conducting membrane.  $\text{La}(\text{Ca}, \text{Ce}, \text{Sm}, \text{Pr}, \text{Gd}, \text{Nd})\text{Fe}(\text{Mn}, \text{Ni}, \text{Al}, \text{Cr}, \text{Mg})\text{O}_{3-x}$  and  $\text{La}(\text{Ca}, \text{Ce}, \text{Sm}, \text{Pr}, \text{Gd}, \text{Nd})\text{Co}(\text{Mn}, \text{Ni}, \text{Al}, \text{Cr}, \text{Mg}, \text{Fe})\text{O}_{3-x}$  powders of varying compositions can be synthesized by mixing high purity precursors of carbonates and oxides in appropriate stoichiometric ratios and calcining them at a temperature of about 1200° C. to about 1300° C. for about 4 hours in air, as known. The calcined powders can be lightly crushed and the calcination step can be repeated to complete the solid-state reaction.

**[0042]** In yet another embodiment, the oxygen-producing material of the second electrode may be a composite material including an electronically conducting oxide and a stabilized zirconia.

**[0043]** The oxygen-producing material of the second electrode can alternatively include a carbonaceous substance that can form a carbon oxide upon oxidation of the oxygen ion, e.g., carbon dioxide and/or carbon monoxide. For instance, the carbonaceous material may be produced by molding petroleum coke and coal tar pitch followed by heat treatment at about 1000° C. to about 1200° C.

**[0044]** As illustrated in FIG. 1, the second electrode 6 can be in the form of a porous layer on the oxygen ion conducting membrane 8. For instance, the second electrode 6 can be applied as a layer, coating, or film on the oxygen ion conducting membrane 8 via a suitable technique such as flame spraying, plasma spraying, sputtering, evaporation, laser ablation, chemical vapor deposition, spray deposition, molecular beam epitaxy, or any other suitable application technique. In another embodiment, the second electrode 6 can be formed as a thin membrane or film and can be laminated to the oxygen ion conducting membrane 8.

**[0045]** The porosity of the second electrode 6 can be suitable to allow diffusion of the molecule oxygen species that is formed at the anode. For instance, the second electrode can

have a porosity of about 50% or less, or from about 20% to about 40% in one embodiment.

**[0046]** The current collector 12 of the second electrode 6 can include any suitable conductive material a is known in the art such as, and without limitation, iridium or other noble metals such as platinum or a solid (non-porous) sintered rod of the aforementioned anode material (electronic oxides, cermets and electronic oxide composites).

**[0047]** During operation, a voltage potential that is greater than the dissociation potential of the metal oxide can be placed across the first and second electrodes 2, 6, via the current collectors 10, 12. Any method or device as is generally known in the art may be utilized to control the voltage potential across the first and second electrodes of the electrochemical cell. In general, the voltage potential for the reaction can be about 30 volts or less. For instance from 0 V to about 30 V or from about 5 V to about 30 V in some embodiments. It should be understood, however, that higher voltages can be possible in some embodiments, as the preferred voltage potential can depend on a plurality of parameters including the electrode spacing as well as the thickness of the solid oxide membrane. For instance, if the electrodes are spaced far apart and/or if the solid oxide membrane is significantly thicker, the voltage potential may be greater than about 30V.

**[0048]** The electrochemical cell of FIG. 1 includes a surrounding tank 18 that can be formed of any suitable insulative or conductive material and in any suitable configuration. For example, the tank 18 can be formed of a coated steel or other metallic material or a polymeric material that can withstand the operating conditions and components of the system. Temperature control elements such as coils, etc. (not shown in FIG. 1) can be associated with the tank 18 to control the temperature of the electrolyte 4, as is known. The temperature of the galvanic cell during operation can be from about 300° C. to about 1000° C., or from about 300° C. to about 800° C., in one embodiment.

**[0049]** A second embodiment of an electrochemical cell is illustrated in FIG. 2. In this embodiment, the oxygen ion conducting membrane 208 in the form a container 208 that can hold the electrolyte 204. The second electrode 206 is in electrical communication with the oxygen ion conducting membrane 208 and the first electrode 202 is immersed in the electrolyte 204 that also carries an oxygen ion conducting compound as discussed above. The first current collector 210 and the second current collector 212 are in electrical communication with one another such that a voltage potential can be placed across the cell that is greater than the dissociation potential of the metal oxide of the first electrode 202. As can be seen, upon oxidation of the oxygen ion at the second electrode 206 a molecular oxygen species can be released from the electrochemical cell as at 214, as discussed above for the electrochemical cell of FIG. 1.

**[0050]** Following dissociation and reduction of the metal oxide to form pure metal in place of the metal oxide of the first electrode, the first electrode can be removed from the cell for recovery of the metal. Another electrode including a metal oxide can then be immersed in the electrolyte, and the process can be repeated.

**[0051]** The recovered metal can be processed for recovery as desired. For example, metallic uranium can be converted to metallic uranium in pellets, ingots, or other forms and in one particular embodiment, uranium as may be utilized as a fuel. The recovered metal can also be mixed with other metallic species to form a mixture of metals or alloy. In one embodi-

ment, recovered uranium can be mixed with other metallic fission products including but not limited to actinides such as plutonium, neptunium, americium, and curium. In one particular embodiment, the mixture of metals including the recovered uranium could be used as fuel.

**[0052]** The process may be better understood with reference to the Example set forth below.

#### EXAMPLE

**[0053]** An electrochemical cell as described herein and schematically illustrated in FIG. 3 was utilized to reduce  $\text{CeO}_2$  as a surrogate of used nuclear fuel to yield a metallic product. The  $\text{CeO}_2$  was chopped and located in a basket formed of graphite that was immersed in one of a variety of electrolytes mixed with 3 wt. %  $\text{Li}_2\text{O}$  based on the weight of the electrolyte. The current collector formed of metallic tungsten was immersed in the  $\text{CeO}_2$ . A yttria stabilized zirconia (YSZ) membrane coated on a surface with platinum was formed into a tube with the platinum on the interior of the tube and isolated from the electrolyte was immersed in the electrolyte as shown as the second electrode. A voltage potential was placed across the first and second electrode to initiate dissociation of the  $\text{CeO}_2$  and reduction of the cerium.

**[0054]** FIG. 4 illustrates the change in electric potential of the cell with temperature for several of the different electrolytes. This diagram shows the equilibrium potentials with temperature, i.e., the potential that would need to be applied for the desired reaction to occur at any temperature, the required potential being greater than the difference between the  $\text{Li}_2\text{O}$  oxygen evolution potential and the potential for the specific oxide to be reduced. The simulations were calculated assuming that  $\text{Li}_2\text{O}$  was the oxygen carrier and that the oxygen was being evolved from  $\text{Li}_2\text{O}$ .

**[0055]** FIG. 5 illustrates the change in cell current and charge of the cell with time with a lithium chloride electrolyte, and FIG. 6 illustrates the oxygen level determined at the oxygen meter (see FIG. 3) with time utilizing a lithium chloride electrolyte. As can be seen, there was a large increase in the current near 4.5 hours (FIG. 5), which indicated reduction of the  $\text{CeO}_2$ . This is believed to correspond to a slower incubation period for the first 4.5 hours during which the outer surface of the  $\text{CeO}_2$  pellets were initially reduced. Following this incubation period, cerium metal that has replaced the  $\text{CeO}_2$  has begun to be formed, and the conductive phase of the electrode has increased in effective area, leading to the increase in cell current shown and increased rate of metal formation. This is also supported by the spike in oxygen generation at the same time shown in FIG. 6. Molecular oxygen was produced at the second electrode during the entirety of the run, and the oxygen detector was saturated after 1 to 1.5 hours following initiation of the experiment.

**[0056]** This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they include structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

What is claimed is:

1. An electrochemical cell comprising:
  - a first electrode including a solid metal oxide and a first current collector;
  - a second electrode including a material that encourages the oxidation of oxygen ion and a second current collector, the first and second electrodes being in electrical communication with one another;
  - an electrolyte comprising an alkali metal or alkaline earth metal salt or a eutectic or mixture thereof;
  - an oxygen ion conducting compound mixed with the electrolyte;
  - an oxygen ion conducting membrane separating the electrolyte from the second electrode.
2. The electrochemical cell of claim 1, the solid metal oxide including uranium oxide.
3. The electrochemical cell of claim 1, the solid metal oxide including an oxide of a noble metal.
4. The electrochemical cell of claim 1, wherein the metal oxide is chopped, ground, porous.
5. The electrochemical cell of claim 1, wherein the metal oxide is held in a container.
6. The electrochemical cell of claim 1, wherein the electrolyte includes a chloride salt of sodium, potassium, lithium, magnesium, calcium, aluminum, or a fluoride salt of sodium, potassium, lithium, magnesium, calcium, aluminum, or cryolite or a mixture or eutectic thereof.
7. The electrochemical cell of claim 1, wherein the oxygen ion conducting compound comprises an alkali metal oxide or alkali earth metal oxide.
8. The electrochemical cell of claim 1, wherein the oxygen ion conducting compound comprises lithium oxide.
9. The electrochemical cell of claim 1, wherein the oxygen ion conducting compound comprises a metal oxide that is the same as the solid metal oxide of the first electrode.
10. The electrochemical cell of claim 1, wherein the oxygen ion conducting membrane comprises a solid composition including one or more oxides containing divalent and/or trivalent cations and one or more oxides containing tetravalent cations.
11. The electrochemical cell of claim 10, wherein the oxygen ion conducting membrane comprises zirconia or hafnia stabilized in cubic form by one or more of  $\text{MgO}$ ,  $\text{NiO}$ ,  $\text{SrO}$ ,  $\text{CaO}$ ,  $\text{NiO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Ce}_2\text{O}_3$ .
12. The electrochemical cell of claim 1, wherein the oxygen ion conducting membrane is immersed in the electrolyte.
13. The electrochemical cell of claim 1, wherein the oxygen ion conducting membrane is a container and contains the electrolyte in the interior of the container.
14. The electrochemical cell of claim 1, wherein the material that encourages the oxidation of oxygen ion comprises platinum, a noble metal, a silver alloy, a cermet, an electronic oxide, a composite thereof stabilized with zirconia, or a carbonaceous substance.
15. The electrochemical cell of claim 14, wherein the material that encourages the oxidation of oxygen ion comprises platinum.
16. The electrochemical cell of claim 1, wherein the second electrode is porous.
17. The electrochemical cell of claim 1, wherein the second electrode is a layer on the oxygen ion conducting membrane.
18. A method for recovering a metal from a metal oxide comprising:

locating a first electrode in an electrochemical cell, the electrochemical cell comprising the first electrode including a solid metal oxide and a first current collector, a second electrode including a material that encourages the oxidation of oxygen ion and a second current collector, an electrolyte comprising an alkali metal or alkaline earth metal salt or a eutectic or mixture thereof, an oxygen ion conducting compound mixed with the electrolyte, and an oxygen ion conducting membrane separating the electrolyte from the second electrode;

applying a voltage potential across the first and second electrodes, wherein the voltage potential is greater than the dissociation potential of the metal oxide of the first electrode, the voltage potential driving a reaction of the metal oxide to form oxygen ions and a solid metal in the place of the solid metal oxide of the first electrode, the oxygen ions being conducted across the electrolyte via the oxygen ion conducting compound and across the oxygen ion conducting membrane to the second electrode, the oxygen ions being oxidized to form a molecular oxygen species at the second electrode.

**19.** The method of claim **18**, wherein the solid metal oxide comprises uranium oxide.

**20.** The method of claim **19**, wherein the uranium oxide is a component of spent nuclear fuel.

**21.** The method of claim **18**, wherein the reaction of the metal oxide includes the formation of a Magneli phase in the metal oxide.

**22.** The method of claim **18**, further comprising following formation of the solid metal in the place of the solid metal oxide removal of the first electrode from the electrochemical cell.

**23.** The method of claim **22**, further comprising locating a third electrode in the electrochemical cell in place of the first electrode, the third electrode comprising a solid metal oxide and a current collector, and thereafter applying the voltage potential across the third electrode and the second electrode,

**24.** The method of claim **18**, further comprising pre-processing the metal oxide prior to locating the first electrode in the electrochemical cell,

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