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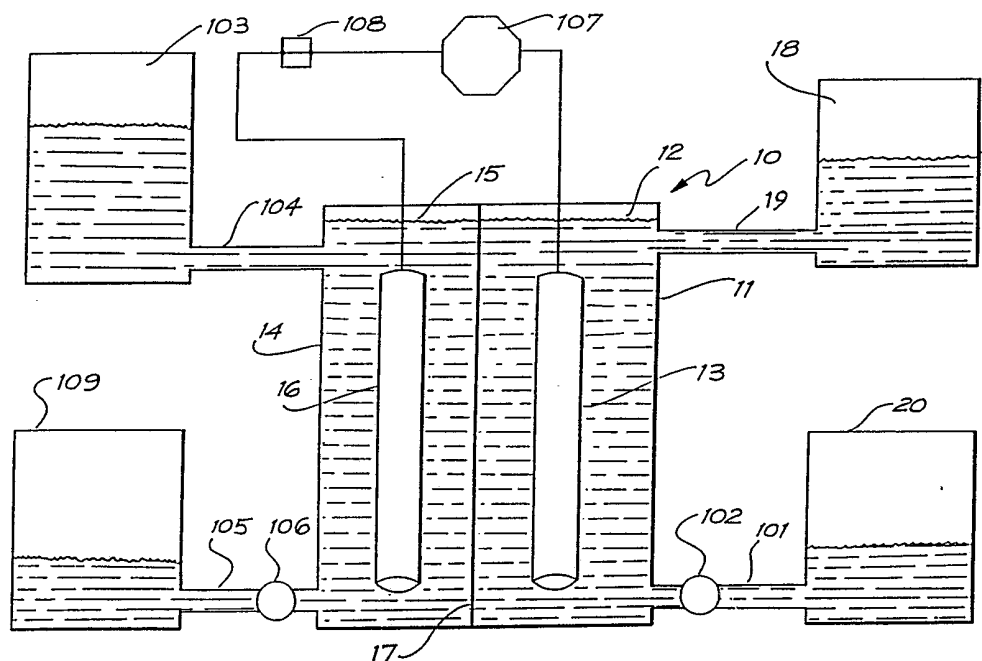
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<p>(21) International Application Number: PCT/AU88/00473</p> <p>(22) International Filing Date: 9 December 1988 (09.12.88)</p> <p>(31) Priority Application Numbers: PI 5849 PJ 0583</p> <p>(32) Priority Dates: 10 December 1987 (10.12.87) 23 September 1988 (23.09.88)</p> <p>(33) Priority Country: AU</p> <p>(71) Applicant (for all designated States except US): UNISE-ARCH LIMITED [AU/AU]; 221-227 Anzac Parade, Kensington, NSW 2033 (AU).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : SKYLLAS-KAZACOS, Maria [AU/AU]; KAZACOS, Michael [AU/AU]; 54 The Esplanade, Sylvania Heights, NSW 2224 (AU). McDERMOTT, Rodney, John, Charles [AU/AU]; 13 Ozone Street, Harbord, NSW 2096 (AU).</p>	<p>(74) Agent: SPRUSON & FERGUSON; GPO Box 3898, Sydney, NSW 2001 (AU).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published <i>With international search report.</i></p>	

(54) Title: VANADIUM CHARGING CELL AND VANADIUM DUAL BATTERY SYSTEM

(57) Abstract

An all-vanadium redox charge cell is disclosed. The cell has a negative charge compartment having a negative charge electrode for charging a charge anolyte in electrical contact with said negative charge electrode; the charge anolyte comprising an electrolyte containing trivalent and/or tetravalent vanadium ions, a positive charge compartment having a positive charge electrode for charging a charge catholyte in electrical contact with said positive charge electrode, the charge catholyte comprising an electrolyte containing tetravalent vanadium ions, and an ionically conducting charge separator disposed between the positive and negative charge compartments to provide ionic communication

between the charge catholyte and the charge anolyte. The positive charge electrode is selected such that it is stable in the charge catholyte in the charge potential range during oxidation of tetravalent vanadium ions to pentavalent vanadium ions at the positive charge electrode and the negative charge electrode is selected such that it is stable in the charge anolyte in the charge potential range during reduction of tetravalent and trivalent vanadium ions to divalent vanadium ions at the negative charge electrode. Also disclosed is an all-vanadium redox dual battery system which incorporates the above all-vanadium redox charge cell.



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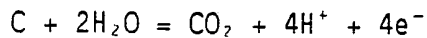
VANADIUM CHARGING CELL AND VANADIUM DUAL BATTERY SYSTEM

TECHNICAL FIELD

This invention relates to an all-vanadium redox charge cell and an all-vanadium redox dual battery system.

BACKGROUND ART

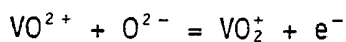
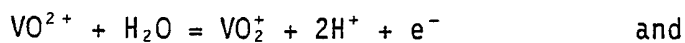
The cycle life of an all-vanadium redox flow battery which uses a positive carbon electrode is currently limited by the slow disintegration of the positive carbon or graphite electrode during charging. This disintegration is postulated to be mainly due to the slow side reaction:



which occurs during oxygen evolution as well as the reaction between the carbon surface and evolved oxygen.

This problem can be alleviated to some extent by avoiding overcharge and restricting the battery charging to up to about 90% state-of-charge.

Another cause of the degradation problem has been postulated to be associated with the vanadium charging reactions described by:



During the oxidation of V (IV) to V (V), oxygen transfer occurs and it has been postulated that oxygen bridging with the electrode substrate is involved. Hence at a carbon electrode it is further postulated that C-O bonds would be broken at the surface when V (IV) is oxidized to V (V) and this in turn leads to disruption of the carbon surface structure and disintegration.

Although the present inventor have found that stability of the positive carbon electrode can be improved during cycling by addition of stabilizing and/or kinetic enhancing ions to the catholyte disintegration of the positive electrode would still occur if the redox battery were permitted to go into overcharge.

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OBJECT OF INVENTION

An object of this invention is to provide an all-vanadium redox charge cell and an all-vanadium redox dual battery system.

DISCLOSURE OF INVENTION

In this specification when reference is made to the electrolytes of the all-vanadium redox charge cell the positive and negative electrolytes are referred to as the catholyte and anolyte respectively. This is opposite to normal convention used in electrolytic processes but for convenience and consistency with nomenclature relating to other all-vanadium redox battery patent applications by the present applicant, the former arbitrary convention has been adopted.

According to a first embodiment of this invention there is provided an all-vanadium redox charge cell having:

a negative charge compartment having a negative charge electrode for charging a charge anolyte in electrical contact with said negative charge electrode, the charge anolyte comprising an electrolyte containing trivalent and/or tetravalent vanadium ions;

a positive charge compartment having a positive charge electrode for charging a charge catholyte in electrical contact with said positive charge electrode, the charge catholyte comprising an electrolyte containing tetravalent vanadium ions; and

an ionically conducting charge separator disposed between the positive and negative charge compartments to provide ionic communication between the charge catholyte and the charge anolyte ; and

wherein the positive charge electrode is stable in the charge catholyte in the charge potential range during oxidisation of tetravalent vanadium ions to pentavalent vanadium ions at the positive charge electrode and the negative charge electrode is stable in the charge anolyte in the charge potential range during reduction of tetravalent and trivalent

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vanadium ions to divalent vanadium ions at the negative charge electrode.

The positive and negative charge electrodes can be any shape desired. It is preferred that the positive and negative charge electrodes are rectangular-plate shaped.

The positive and negative charge electrodes are chosen from electrode materials which are stable in the charge catholyte and charge anolyte respectively in the potential ranges in which the respective charge reactions occur.

The negative charge electrode has a higher hydrogen overvoltage than copper to minimise H_2 evolution during the charging reaction at the positive charge electrode. Low H_2 evolution during charging means low volume water loss from the cell electrolyte, low risk of H_2 explosion and high coulombic charging efficiency at the negative charge electrode. The negative charge electrode can be selected from the group consisting of Tl; Bi; Pb; Hg; In; Cd; Ag; Ga; Sb; Zn; Pb/Hg; Pb/Bi; Hg/In; Hg/Cd; Hg/Ga; Hg/Ag; carbon and graphite felt, mat, plate, rod, knit, fibre, and cloth; carbon impregnated teflon; carbon impregnated polyethylene; carbon impregnated polypropylene; carbon impregnated polystyrene; carbon impregnated polyvinylchloride; carbon impregnated polyvinylidenechloride; glassy carbon; non-woven carbon fibre material; and cellulose (most of the metallic materials could not be used to discharge the negative half-cell because they will corrode or passivate at the discharge potentials). In an all-vanadium redox charge cell in which the charge anolyte comprises 2M trivalent/tetravalent vanadium ions in 2M - 3M H_2SO_4 and the charge catholyte comprises 2M pentavalent-tetravalent vanadium redox system in 2M - 3M H_2SO_4 , the open circuit potential of the negative charge cell is about -0.4V vs SHE. It is preferable to select the negative charge electrode from electrode materials which are stable to corrosion at the open circuit potential. Whilst some of the preceding negative charge

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electrode materials will dissolve/complex/corrode at open circuit (eg Cd and In) they can still be utilized but in such instances there is a need to continuously apply a suitable negative potential to such materials as they are brought into contact with the anolyte, so that the potential of the materials is more negative than $-0.4V$ vs SHE, thus preventing the materials from corroding.

The inventor has found surprisingly that many materials are unsuitable for use as a positive charge electrode and they have also found unpredictably that a number of materials which are suitable for use as the positive charge electrode can be selected from the group consisting of DSA, platinised Ti; platinised Ru; platinised Ir; and V_2O_5 coated on Pb, Ti, Zr, Hf, Ta, W or Nb. The V_2O_5 coated electrodes would be unsuitable for the positive half-cell in a discharging battery as it would dissolve at the discharge potential range. A DSA electrode would perform well for both charging and discharging but it is an expensive electrode material and the lifetime of DSA electrodes is limited as has been found by cycling experiments.

The charge cell of the invention includes monopolar and bipolar type charge cells. A bipolar charge cell typically includes a plurality of positive charge compartments each having a positive charge electrode therein and a plurality of negative charge compartments each having a negative charge electrode therein and wherein each of the compartments are separated by a membrane. A bipolar charge cell is typically of the flat plate- or filter press-type.

The charge cell can include a charge anolyte reservoir for storing charge anolyte operatively coupled to the negative charge compartment by charge anolyte supply and return lines via a pump and a charge catholyte reservoir for storing charge catholyte operatively coupled to the positive charge compartment by charge catholyte supply and return lines via a pump.

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In an alternative arrangement the charge cell can include a charge anolyte charge reservoir having charge anolyte charge supply and return line or lines for charging further charge anolyte which is to be delivered to the negative charge compartment and a charge catholyte charge reservoir having charge catholyte charge supply and return line or lines for charging further charge catholyte which is to be delivered to the positive charge compartment an charge anolyte storage reservoir having charge anolyte storage supply and return line or lines for storing charge anolyte from the negative charge compartment and a charge catholyte storage reservoir having charge catholyte storage supply and return line or lines for storing charge catholyte from the positive charge compartment and pumping means operatively coupled to the charge anolyte storage line or lines and/or the charge anolyte charge line or lines and to the charge catholyte storage line or lines and/or the charge catholyte charge line or lines for pumping:

(i)the charge catholyte through the charge catholyte storage line or lines, the positive charge compartment and the charge catholyte charge line or lines; and

(ii)the charge anolyte solution through the charge anolyte solution storage line or lines, the negative charge compartment and the charge anolyte solution charge line or lines.

According to a second embodiment of this invention there is provided a process for charging a charge anolyte and a charge catholyte of an all-vanadium redox charge cell having:

a negative charge compartment containing a charge anolyte and having a negative charge electrode for charging said charge anolyte in electrical contact with said negative charge electrode, the charge anolyte comprising an electrolyte containing trivalent and/or tetravalent vanadium ions;

a positive charge compartment containing a charge catholyte and