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## (54) IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL SYSTEMS

(71) We, ACCUMULATORENWERK HOPPECKE ZOELLNER & SOHN, of Barbarossa-platz 2, 5000 Köln, Germany, a Kommanditgesellschaft organised and existing under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to electrochemical systems, in particular metal-air cells, consisting of a consumable electrode, an air electrode and, between the electrodes, an electrolyte.

The term "air electrode", as used herein includes oxygen electrodes or  $H_2O_2$  electrodes; the term "air electrode" is used merely for convenience and is not intended to impart any restriction.

There has been proposed for example in U.S. Patent Specification No. 3,788,899 an electrochemical battery of the above type in which, in order to increase the performance, the temperature of the electrolyte is regulated by warming the electrolyte. However, this is advantageous in that the temperature of the entire electrochemical system is increased through heat exchange between the individual parts. It is also disadvantageous in that the electrolyte becomes substantially more corrosive at increased temperatures and, consequently, the management of the electrochemical system is rendered difficult.

The fundamental difficulty of this previously proposed type of electrochemical battery consists in that only small current densities of about 50 mA/cm<sup>2</sup> can be obtained. Moreover, the duration of the obtainable current densities is narrowly limited, and outputs of about 300 Wh/kg are usually expected. Although increased currents may be obtained by enlarging the electrode surface, the current density nevertheless still remains very low, which is necessary in order to keep polarisation effects small.

According to the invention, there is provided a process for producing high output

with high current densities in an electrochemical system comprising a consumable electrode, an air electrode, and an electrolyte between the electrodes, wherein the heat occurring at the interphase between the electrolyte and the consumable electrode is retained in the interphase whereby a high temperature in relation to the temperature of the system as a whole, is created locally.

Further according to the invention, there is provided an electrochemical system comprising a consumable electrode, an air electrode, and an electrolyte between the electrodes, in use of the system a high temperature in relation to the temperature of the system as a whole being established locally at the interphase between the consumable electrode and the electrolyte.

Thus, instead of bringing the entire electrochemical temperature in order to achieve high performance, a localized zone of the system is brought to the most favourable temperatures in order to achieve the specific objectives. Consequently, only the effective temperature accessory for the attainment of high performance with high current densities is set up in the electrode/electrolyte interphase.

In electrochemical reactions, conversions take place which proceed in purely chemical manner so that heat is generated at, or in the immediate proximity of, the actual reaction point. Depending on the distribution of this heat, i.e. the manner in which it is given off to the surroundings, the temperature of the reaction point which lies in the electrode/electrolyte interphase may lie considerably above the temperature of the surroundings, that is to say, on the one hand, the electrolyte and, on the other hand, the main part of the electrode body, at some distance from the reaction point.

The temperature in the interphase of the consumable electrode with the electrolyte may be sufficiently high that local fusion and/or softening of the electrode material occur. On the other hand, it may also be expedient to remove the heat present at the interphase of the air electrode with the elec-

trolyte and to set up locally a low temperature in comparison with that of the system as a whole. The parameters for the local heating and (if provided) cooling of the interphases and, hence, of the reaction zone of the electrochemical system, are the heat capacities and thermal conductivities of the relevant components of the system which are in immediate contact with the reaction point.

In a preferred embodiment of the invention the area of the consumable electrodes contacted by the electrolyte be kept small and those surfaces of the consumable electrode which give off heat are likewise kept small and/or insulated in order to reduce the dissipation of heat to the surroundings. It is in this way possible substantially to increase locally the interphase temperature at the consumable electrode in comparison with the temperature of the system as a whole.

The temperature of the reaction zone may be influenced by using highly electropositive metals in compact form, preferably aluminum. The material of the consumable electrode may also be alloyed with substances which, in comparison with the actual electrode material, have a high relative with the electrolyte, in particular with alkali metals and/or alkaline earth metals. The temperature of the phase boundary is in this way increased artificially. With increasing temperature in this boundary layer, the current densities obtained also become higher, for the same potential of the working electrode. To the electrode material there may also be added substances which act as catalysts for heat-generating reactions which increase the surface temperature of the consumable electrode in the interphase.

By using the above effects it is possible to change over from highly porous electrodes such as sinter electrodes, suspension electrodes or sedimented electrodes previously proposed for the purpose of enlarging the surface, to commercially-available compact metals as electrodes, without having to forego the achievement of high current densities. A consumable electrode consisting of compact metal can be produced in a simple manner and can simply be incorporated into an electrochemical cell, is economical and also facilitates conductivity. Advantageously the electrode may be a rod-shaped, for example cylindrical, electrode in which the ratio of the radius to the length of the rod determines the operating temperature on the reaction surface. A rod-shaped consumable electrode renders possible in particularly simple manner the heat control or temperature control in the electro/electrolyte interphase.

From this electrode form there may also be derived plate-type electrodes by the elec-

trode length being kept small compared with its diameter.

It may be advantageous to control the heat/temperature in the electrode/electrolyte interphase not through metallurgical, chemical or constructional measures but, instead, by locally heating the consumable electrode and cooling the air electrode. This may be effected for example by a medium which flow around the electrode or by using heating elements. It has been found that warming the electrode to certain temperatures for the purpose of controlling the temperatures at the reaction zone leads to favourable energy density values independently of the temperature of the electrolyte. Thus, for example with a rod-shaped aluminium electrode which is warmed to 80°C, results can be obtained at electrolyte temperatures of 16°C which are better than those of the same electrode warmed to 70°C with an electrolyte also at 70°C.

With the high current densities which can be achieved correspondingly much matter of the consumable electrode is degraded. In order to transport away from the reaction zone the substances which are degraded to a large extent and to supply sufficient reactants to the reaction zone, the electrolyte may be supplied to and removed from the interphase only. By using electrolyte flow to the interphase only, there is also prevented the formation, at the electrode surface, of a stationary electrolyte layer which, through processes caused by diffusion, slows down the reaction and thus lowers the current density which can be obtained. The electrolyte may be cooled by removal of heat and the removed heat may be supplied to an electrode for the local heating of the interphase. Further, in the case of the high current densities, that is to say high currents for the cell, it is preferred to reduce the ohmic losses as far as possible, which can be done by keeping small, and constant, the spacing of the two electrodes from one another. The distance between two electrodes of an electrochemical cell can be kept constant by pushing the consumable electrode in order to advance the electrode. For special purposes, for example one-trip cells, which have to fulfil their energy-supplying function for a relatively short time, it is not necessary to advance the electrode since the electrode mass carried away during use does not excessively prolong the electrolytic route. By means of the heat control or temperature control in the interphase the high performance can nevertheless be substantially retained throughout the working life, even with increasing electrode spacing.

The invention will now be described, by way of example only, with reference to the

accompanying driagrammatic drawings, in which:

Figure 1 shows, schematically, a metal-air cell;

5 Figure 2 shows graphically the dependence of the cell voltage on the current density;

Figure 3 shows graphically the dependence of the output on the current density;

10 Figure 4 shows graphically the dependence of the voltage on the current density;

Figure 5 shows graphically the dependence of the current density as a function of the potential of an aluminium electrode of the cell as different temperatures of the latter.

15 In Figure 1 only the basic components of the metal-air cell are shown; such a cell is described in greater detail in our Patent Specification No. 1513940. The cell comprises a consumable electrode in the form of a cylindrical aluminium electrode 1 having a purity of 99.8%, a diameter of about 20 mm, and a length of about 50 mm. Opposite the aluminium electrode 1 is an oxygen electrode 4 arranged at a distance of about 1 mm. Between the opposed surfaces 2 and 5 of the aluminium electrode 1 and the oxygen electrode 4, electrolyte 3 is moved in constant circulation.

65 Curve 1 corresponds to: AL 5 N, the consumable electrode and the electrolyte are at a temperature of 70°C.

70 Curve 2 corresponds to: Al 5 N, water at a temperature of 80°C flows around the consumable electrode, and the electrolyte is kept at a temperature of 20°C.

75 Curve 3 corresponds to: Al 5 N, the consumable electrode and the electrolyte are at a temperature of 20°C.

Curve 4 corresponds to: Al 5 N, the consumable electrode is at a temperature of 20°C and the electrolyte is at a temperature of 70°C.

80 From these curves it will be seen that an increase in the temperature of the electrolyte alone, from 20°C to 70°C (curves 3 and 4) produces no significant improvement but a considerable improvement is associated by increasing the temperature of the consumable electrode alone from 20°C to 80°C (curve 2). This is confirmed by curve 1 in which, with the electrode temperature (70°C) remaining about the same compared to curve 2, the electrolyte temperature is increased to 70°C. However, at high electrolyte temperatures, the KOH is very corrosive over long periods and practically the same results (but without the corrosion) can

At an electrolyte temperature of about 20°C and an electrode temperature of the aluminium electrode 1 of about 90°C, current densities of up to a maximum of 5 A/cm<sup>2</sup> were measured without separation of hydrogen. In the case of lower current densities, output densities of up to 1.3 W/cm<sup>2</sup> were reached.

Figure 2 shows graphically the dependence of the cell voltage V on the current density, measured in A/cm<sup>2</sup> for an arrangement generally similar to that of Figure 1 in which the electrolyte is kept at a temperature of 60°C and the aluminium electrode, differently from that which occurs in the above embodiment, can give off heat to the ambient air at room temperature. The curve makes clear that very high current densities are obtained together with good voltage values and a high energy yield.

Figure 3 shows graphically the relationship between output and the current density for the conditions described with reference to Figure 2.

Figure 4 shows graphically the voltage against current density, determined according to potentiodynamic methods 100 mV/min., in KOH 6.5 M at electrolyte in which the potential of the aluminium electrode is measured and the current density is contrasted, for different conditions within the cell.

be achieved by the conditions associated with curve 2.

In the graph of Figure 5, the four curves relate to the following measured values:

Curve 1: KOH 39°C, aluminium electrode 8.5°C;  
Curve 2: KOH 40°C, aluminium electrode 22°C;  
Curve 3: KOH 40°C, aluminium electrode 30°C; and  
Curve 4: KOH 40°C, aluminium electrode 60°C.

It will be seen that, in the manner des-

cribed, high outputs with high current densities can be produced over a long period, without warming the electrolyte and without the natural voltage of the electrode having to be reduced in the manner which is now usual. With moderate electrolyte temperatures, energy densities can be achieved which, hitherto, can otherwise be attained only with high-temperature cells.

#### WHAT WE CLAIM IS:—

1. A process for producing high output with high current densities in an electrochemical system comprising a consumable electrode, an air electrode, and an electrolyte between the electrodes, wherein the heat occurring at the interphase between the electrolyte and the consumable electrode is retained in the interphase whereby a high temperature in relation to the temperature of the system as a whole, is created locally.

2. A process according to claim 1, wherein the temperature in the interphase of the consumable electrode with the electrolyte is such that local fusion and/or softening of the electrode material occur.

3. A process according to claim 1 or claim 2, wherein the area of the consumable electrode contacted by the electrolyte is kept small.

4. A process according to any one of claims 1 to 3, wherein the surfaces of the consumable electrode which give off heat are kept small and/or are insulated.

5. A process according to any one of claims 1 to 4, wherein the heat generation in the interphase is increased by the use of highly electropositive metals in compact form.

6. A process according to claim 5, wherein the material of the consumable electrode is alloyed with substances which have a high reactivity with the electrolyte.

7. A process according to any one of claims 1 to 6, wherein the consumable electrode is heated, and/or the air electrode is cooled.

8. A process according to any one of claims 1 to 8, wherein the electrode is in the form of a cylindrical rod.

9. A process according to any one of claims 1 to 8, wherein the electrolyte is supplied to, and removed from, the interphase only and is at approximately room temperature.

10. A process according to any one of claims 1 to 9, wherein the electrolyte is cooled by removal of heat and the removed heat is supplied to the consumable electrode for local heating of the interphase.

11. A process according to any one of claims 1 to 10, wherein the two electrodes are closely spaced by a constant distance.

12. A process according to any one of claims 1 to 11, wherein that the heat present at the interphase of the air electrode with the electrolyte is removed and a low local temperature in comparison with that of the system as a whole is provided.

13. An electrochemical system comprising a consumable electrode, an air electrode, and an electrolyte between the electrodes, in use of the system a high temperature in relation to the temperature of the system as a whole being established locally at the interphase between the consumable electrode and the electrolyte.

14. A process according to claim 1, substantially as hereinbefore described with reference to the accompanying drawings.

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FIG.1

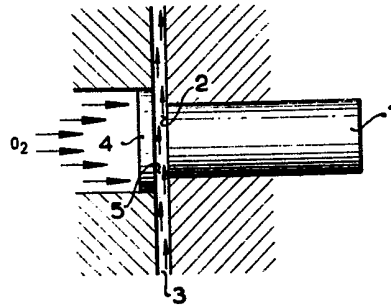


FIG.2

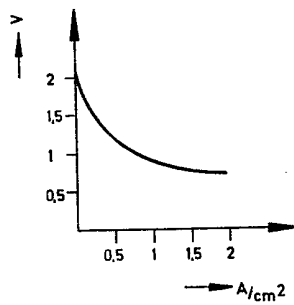


FIG.3

