

Optimization studies on a Fe/Cr redox flow battery

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(Received November 15, 1991)

Abstract

The performance of a Fe/Cr redox flow battery which operates in bipolar mode is described. The optimization studies on electrolyte composition, temperature and membrane type are presented. These studies have achieved a coulombic efficiency of 97% and an energy efficiency of 73% for an electrolyte composition of 2.3 M HCl+1.25 M FeCl₂+1.25 M CrCl₃, working at 44 °C with a current density of 40 mA/cm² and using the Nafion 117 membrane. A maximum discharge power density of 73 mW/cm² has been obtained.

Introduction

In 1974, the concept of an electrochemical storage system based on a redox flow cell was presented by Thaller [1]. This concept is based on the storage of two fully-soluble redox couples which are continuously pumped through a power conversion cell.

The unity cell consists of two electrodes separated by an ion-exchange membrane. The role of these electrodes is to play as simple electron exchangers for the electrochemical reactions occurring on their surface.

One of the most important features of this kind of battery is the possibility of an independent scaling-up of the electric energy storage section (external tanks) and the power section (electrochemical cell). Moreover, these batteries have no life cycle limitation and their cost would be low for a large-scale production. Their main disadvantage is the lower energy storage density in comparison with other batteries (lead/acid, Ni/Cd, etc). For this reason, this kind of system is more attractive as a mass storage device for load-leveling and stand-alone applications.

In the Fe/Cr redox battery, the electrolytes involved are two identical solutions of FeCl₂ and CrCl₃ in HCl medium (mixed reactant mode). The charge process causes the oxidation of the Fe(II) species to Fe(III) in the positive half-cell, and the reduction of the Cr(III) species to Cr(II) in the negative half-cell. When the battery is in discharge operation, these processes are reversed.

The Fe(III)/Fe(II) couple has a suitable electrochemical reversibility on carbon and graphite electrodes. However, a catalyst is needed on the negative half-cell due to the irreversibility of the Cr(III)/Cr(II) couple on these kind of electrodes. Moreover, hydrogen evolution appears as a competitive reaction to the reduction of the Cr(III) species. This hydrogen evolution produces a decrease in the coulombic efficiency of the system and an unbalance between the states-of-charge of the two electrolytes. A

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rebalance cell must be used to maintain these states-of-charge at the same level. In this cell, the reduction of the Fe(III) species occurs as cathodic reaction and the oxidation of the chloride ions to chlorine (or other convenient reaction) occurs as anodic reaction.

The behaviour of a redox flow cell may be evaluated by its voltage, current and density efficiencies. The voltage efficiency (η_v) is defined as the ratio between the discharge and charge voltages, measured at a given state-of-charge (normally 50%). The coulombic efficiency (η_c) is defined as the ratio charge between that given by the battery and the charge introduced in it between two defined states-of-charge. The energy efficiency may be evaluated in two ways: (i) as the ratio of the energy given by the battery and the energy introduced between two defined states-of-charge, and (ii) as the product of the voltage and coulombic efficiencies for a given state-of-charge. The first criterion has been chosen.

Due to the better energy efficiency of high-voltage low-current devices for power transmission, batteries are usually arranged in bipolar assemblies with parallel electrolyte feeding.

In this paper the optimization of a bipolar system is studied. Factors affecting voltaic and coulombic losses including electrolyte composition, temperature and cell separators are presented.

Experimental

A schematic diagram of the assembly built to evaluate a bipolar system is shown in Fig. 1. The system includes a four-cell bipolar stack, a rebalance cell, two electrolyte tanks and magnetically driven pumps. Electrodes with 215 cm² geometric area were made from a pretreated RVC-4000 (Le Carbone Lorraine) carbon felt and JP845

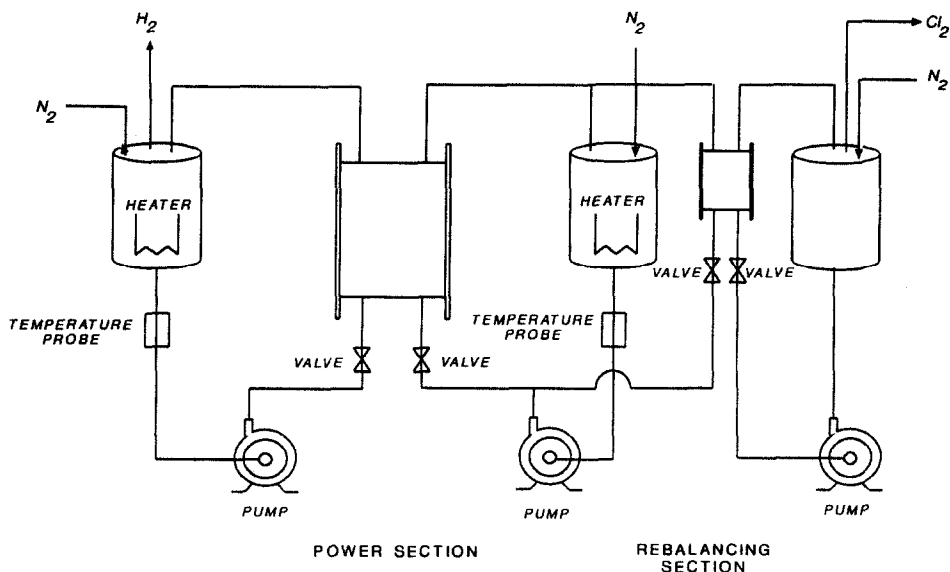


Fig. 1. Scheme of a Fe/Cr redox flow battery.

(Le Carbone Lorraine) graphite plates were used as current collectors. The electrodes were submitted to the following treatments: (i) immersion in methanol during 5 min; (ii) immersion in H_2O_2 during 48 h and washing with water until $\text{pH} \approx 7$.

The electrolyte solutions were 1.25 M FeCl_2 + 1.25 M CrCl_3 in different HCl concentrations. Based on previous studies on the electrocatalysis of the Cr(III)/Cr(II) system [2], PbCl_2 was added in order to enhance Cr(III)/Cr(II) couple reversibility and decrease hydrogen evolution.

PVC frames were used to get a suitable intra-stack electrolyte flow distribution. The geometry of these frames was optimized in order to minimize energy losses due to shunt currents [3] and pumping power [4, 5]. The optimization studies for shunt-current losses and flow distribution were carried out using the software developed at this Centre based on simulation models reported by several authors [6–14].

The state-of-charge (SOC) of the battery is obtained from the open-circuit cell voltage using a previously made calibration curve. Moreover, the individual electrode potentials versus a saturated calomel electrode (SCE) were recorded and related to the state-of-charge. A Nafion-117 membrane was used as battery separator.

Results and discussion

Study of the behaviour of a bipolar prototype at different HCl concentrations

Kinetic data given by several authors [15–20] show that chloride ions have a double effect on the kinetics of the Cr(III)/Cr(II) couple. First, an increase in chloride ion concentration causes a shift of equilibrium between aquo and aquo-chloride chromium complexes to $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$ and $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ species. These chlorocomplexes undergo a more reversible behaviour than the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ species. Secondly, the adsorption of chloride ion on the electrode surface acts as an effective bridge for the electron transfer.

Therefore, an increase in HCl concentration would be very favourable for the reversibility of the system although it should not be forgotten that an increase in hydrogen ion concentration enhances hydrogen evolution, and diminishes coulombic efficiency.

Therefore, a study of the redox battery behaviour has been carried out along continued charge/discharge cycles between 20 and 80% SOC at 40 mA/cm² current density, using HCl solutions of different concentration, (1.5–3.0 M). The work temperature of the electrolyte was 29 °C.

Variation of the internal resistance of the cell

During the first cycle, the polarization curves in charge and discharge at 50% SOC have been obtained. Cell resistances were measured from the slopes of the charge and discharge polarization curves. The values of the internal resistance of the cell decreases when HCl concentration increases (Table 1(a)).

Variation of hydrogen evolution with the number of cycles

No increase in the volume of the hydrogen evolved is observed when HCl concentration is increased. In each series of experiences, a 0.6% loss of coulombic efficiency is encountered due to hydrogen evolution.

Efficiency variations with the number of cycles

The voltage, coulombic and energy efficiencies obtained in each series of experiences at different HCl concentrations are kept constant through the charge/discharge cycles.

TABLE 1

Experimental data of a bipolar system at different conditions

(a) Electrolyte 1.25 M FeCl ₂ + 1.25 M CrCl ₃ , at 29 °C					
HCl (M)	R_C^a	R_D^a	η_C^b	η_V^b	η_E^b
1.5	4.6	4.7	95	68	65
1.8	4.1	4.2	95	70	66
2.3	3.8	3.9	97	73	70
3.0	3.9	3.8	96	73	70
(b) Electrolyte 1.25 M FeCl ₂ + 1.25 M CrCl ₃ + 2.3 M HCl					
Temperature (°C)	R_C	R_D	η_C	η_V	η_E
20	4.1	4.2	96	71	68
29	3.8	3.9	97	73	70
38	3.7	3.5	96	75	72
44	3.6	3.4	97	76	73
(c) Electrolyte 1.25 M FeCl ₂ + 1.25 M CrCl ₃ + 2.3 M HCl at 29 °C					
Separator	R_C	R_D	η_C	η_V	η_E
CR-2	4.0	4.2	96	72	69
Nafion-117	3.8	3.9	97	73	70
PVC	3.1	3.4	74	77	56

^a R_C and R_D : charge and discharge resistance ($\Omega \text{ cm}^2$).^b η_C , η_V and η_E : coulombic, voltage and energy efficiencies (%).

In Fig. 2 and Table 1(a), average values for the parameters obtained in each series are compared. As can be observed, there is a 96% coulombic efficiency in the 20–80% SOC range.

Voltage efficiency η_V as well as energy efficiency η_E increase with HCl concentration until a maximum value is reached for a 2.3 M HCl solution.

Study of performances of a bipolar prototype at different temperatures

Starting out from an optimum 2.3 M HCl concentration, charge/discharge cycles at different temperatures were performed and a study of the temperature influence on the efficiency of the redox battery was made. The temperature range studied was 20–44 °C.

Figure 3 shows the variation of the battery voltage and power in discharge operation versus current density at 44 °C. The power reaches a maximum value of 73 mW/cm² at 137 mA/cm².

Figure 4 and Table 1(b) show the variation of average coulombic, energy and voltage efficiencies with the temperature for several experiments. The coulombic efficiency is practically constant with the temperature. However, the voltage efficiency increases its value by 5% when the temperature rises from 20 to 44 °C. This fact is due to the

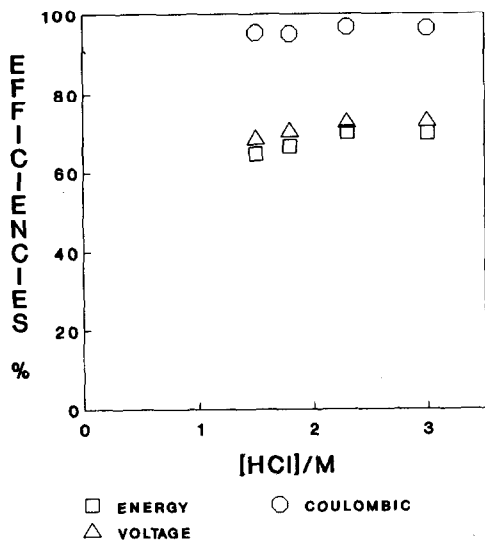


Fig. 2. Variation of battery efficiency with the number of cycles, at current density of 40 mA/cm^2 (charge and discharge modes) at different HCl concentrations.

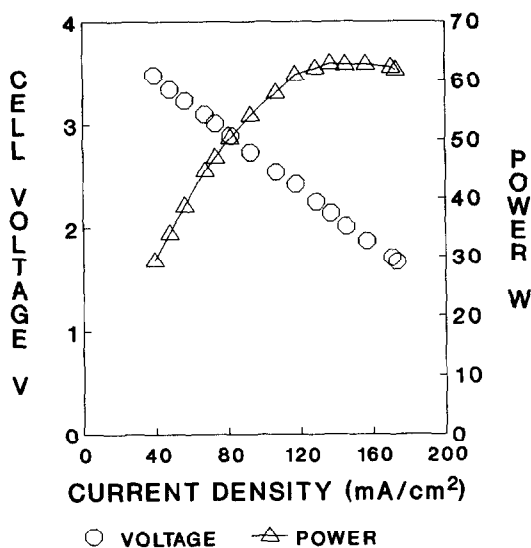


Fig. 3. Variation of battery voltage and power in discharge operation vs. current density at 44°C .

diminution of the internal resistance of the cell from 4.2 (20°C) to $3.4 \Omega \text{ cm}^2$ (44°C) (Table 1(b)). In the same way, energy efficiency is increased by the same percentage.

The charge loss due to hydrogen evolution is not affected by the increase of the temperature.

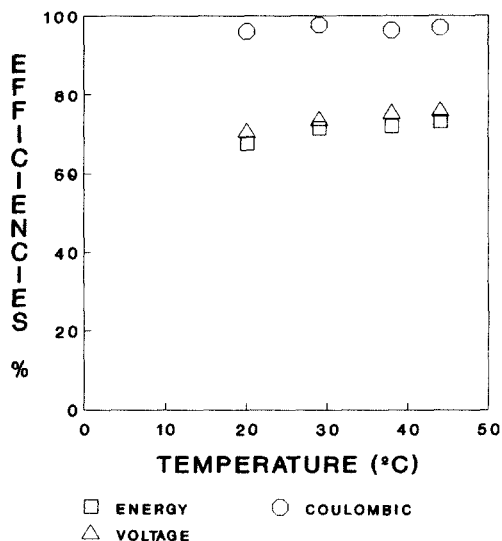


Fig. 4. Variation of battery efficiencies with the number of cycles at a current density of 40 mA/cm^2 (charge and discharge modes) at different temperatures. Supporting electrolyte concentration 2.3 M .

Comparative study of the performance of a bipolar prototype with different membranes and separators

In order to diminish the internal resistance of the cell, the performance of the redox cell has been studied. Cationic membranes Nafion-117, CR-2 (Neosepta) have been used in agreement with the results obtained in previous studies on the resistivity and selectivity of different cationic membranes [21].

The cationic CR-2 membrane has a lower resistivity than the Nafion-117 membrane. Moreover, it is more selective and has a lower cost than this membrane.

In the same way, the performance of the redox cell has also been tested with a nonselective microporous plastic separator (Daramic). This separator has some important advantages such as very low-cost and high-mechanical stability.

The working conditions with the three separators were the same, and the experiments were carried out at $29 \text{ }^\circ\text{C}$.

The values of the internal resistance of the cell for each membrane or separator have been compared in Table 1(c), both for charge and discharge processes. The use of Daramic in the place of Nafion-117 reduces the internal resistance of the cell.

In Fig. 5 and Table 1(c), the redox cell efficiencies during continued charge/discharge cycles are compared for the different membranes and separators used. Both membranes show similar efficiencies but the mechanical resistance of the CR-2 membrane was very poor and for this reason it was rejected. Due to the lower resistance of the separator, the voltage efficiency rises to 77%. However there is an important decrease in the coulombic efficiency employed (74% versus 96% for the membranes). This decrease is mainly due to the higher reactant flow through the separator that produces a bigger self-discharge of the system. This fact leads to an important decrease in energy efficiency being 56% of the average value of this parameter.

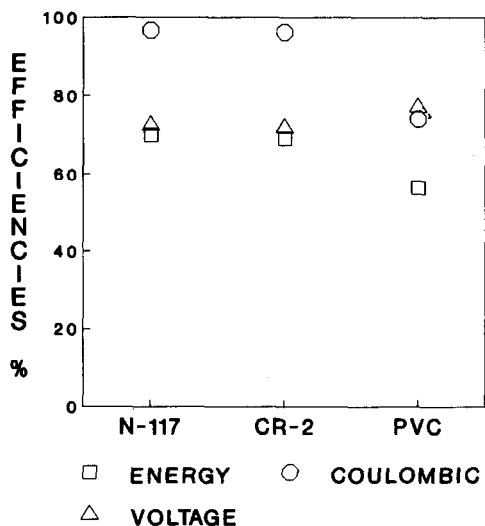


Fig. 5. Comparison of performance of bipolar prototype with different membranes and separators. Supporting electrolyte concentration 2.3 M.

Conclusions

The working conditions of a Fe/Cr redox flow cell have been optimized. The parameters studied were the composition of the supporting electrolyte, the temperature and type of separator of the cell. This study has 97% coulombic efficiency and 73% energy efficiency for 2.3 M HCl concentration using Nafion-117 as separator. A maximum discharge power density of 73 mW/cm² has been obtained.

Acknowledgements

This project is being financed by Hidroelectrica Española S.A. Research and New Energies Department/SEP, Tudor S.A., Universidad de Alicante and EEC (contract No. EC 094/88 ES). The collaboration of J. Medina and M. A. Pastor is also acknowledged.

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