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铁-杂多酸液流电池的研究

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摘要 本文报道的氧化还原流动池, 负极活性物质为 FeSO_4 , 正极为 $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ (HP). 具有选择性的阳离子交换膜将两个经活化的多孔碳毡电极分开, 两个氧化还原电对在碳和石墨电极上都具有相适应的电化学可逆性. 电池的活性物质很稳定, 电池没有使用寿命限制.

关键词 液流电池, 杂多酸, 电源, Fe-HP 液流电池

STUDIES ON AN IRON-HETEROPOLYACID REDOX FLOW BATTERY

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Abstract This paper reports a new Fe-HP redox flow cell. The positive and negative electrodes active materials are phosphomolybdic acid and acidified ferrous sulphate solutions respectively. Two activated porous carbon felt electrodes where the electrochemical reactions take place, are separated by a selective cation-exchange membrane. The both couples have a suitable electrochemical reversibility on carbon and graphite electrodes. The active materials of the cell have very high stability. Moreover the cell has no life cycle limiting.

Key words Redox cell, Heteropolyacids, Power sources, Fe-HP redox cell

1 Introduction

A suitable storage method is a requisite for the utilization of solar, wind or tidal energy in large scale electrical energy production.

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. 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). In addition this spatial separation of transformation and storage, and allows one to choose the energy and power independent of one another during construction of the redox cell. Moreover, these batteries have no life cycle limiting factors, such as shape changes, inactive forms of reactants, and dendrite formation. There are also many advantages in system sizing and control. Their main disadvantage is the lower energy storage density in comparison with other batteries (lead/acid, Ni/Cd, etc). For this reason, this system is more attractive as a mass storage device for load-leveling and stand-alone applications.

The unity cell consists of two electrodes separated by a highly selective anion-exchange membrane. The role of these electrodes is to play as simple electron exchangers for the electrochemical reactions taking place on their surface. Since the redox flow cell concept was proposed, a number of redox couples have been investigated^[2-9]. This paper describes a redox cell, the two redox couples involved are solutions of iron [Fe(III)/Fe(II)] and $\text{PM}_{0.12}\text{O}_{40}^{3-}$ [$\text{PM}_{0.12}\text{O}_{40}^{3-}$ / $\text{H}_n\text{PM}_{0.12}\text{O}_{40}^{3-}$] ($n=2, 4$) in H_2SO_4 medium. The charge process causes the oxidation of the $\text{H}_n\text{PM}_{0.12}\text{O}_{40}^{3-}$ species to $\text{PM}_{0.12}\text{O}_{40}^{3-}$ in the positive half-cell, and the reduction of the Fe(III) species to Fe(II) in the negative half-cell. When the cell is in discharge operation, these processes are reversed. The both couples have a suitable electrochemical reversibility on carbon and graphite electrodes. In addition above mentioned advantage of redox flow, the Fe/HP redox cell has higher energy storage efficiency and stability which has potential for a long cycle life in comparison with Fe/Cr redox cell^[10].

Moreover it has projected lower cost of the cell manufacture in comparison with the vanadium (v(II)/v(III)) redox cell.

The behaviour of a redox flow cell may be evaluated by its voltage, current and energy 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 between charge given by the cell and the charge introduced in it between two defined states of charge. The energy efficiency (η_e) may be evaluated as the product of the voltage and coulombic efficiencies for a given state-of-charge.

2 Experimental Procedure

Material object photograph of a laboratory scale flow cell is shown in Fig. 1. The system includes a unity cell, two electrolyte tanks and magnetically driven pumps. Electrodes with 70 cm^2 geometric area were made from a pretreated carbon felt and graphite plates were used as current collectors. The electrode was submitted to the following treatments: (i) immersion the carbon felt in methanol during 20 min; (ii) immersion in H_2O_2 during 48 h and washing with water until $\text{pH} = 7$. A

polystyrene sulfonic acid type cationic exchange membranes was used in the cell as separator. Polyethylene 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 and pumping power. The electrolyte solutions were $1\text{ mol}\cdot\text{L}^{-1}\text{ FeSO}_4 + 0.5\text{ mol}\cdot\text{L}^{-1}\text{ H}_2\text{SO}_4 + 3\text{ mol}\cdot\text{L}^{-1}\text{ NaSCN}$ and saturated $\text{H}_3\text{PM}_{0.12}\text{O}_{40}$ in $0.5\text{ mol}\cdot\text{L}^{-1}\text{ H}_2\text{SO}_4$.

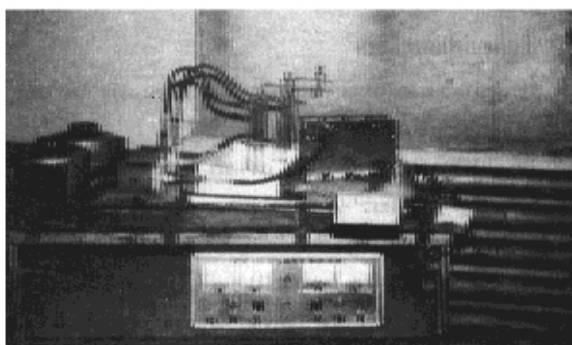


Fig. 1 Photograph of a laboratory-scale flow cell at 25 ± 0.2 charging current $34\text{ mA}/\text{cm}^2$

3 Results and Discussion

1) Characteristics and Performance of the Cell

The cell was performed at ambient temperature. The open-circuit voltage behaviour of the cell is shown in Fig 2, wherein the open-circuit voltages during charge and discharge modes are plotted as a function of state of charge for a complete cycle, flow of the electrolyte was controlled by an average of 200 ml/m in a electrode or so. Fig 2 gives first, tenth and twentieth cycles results that illustrates the stability of the cell during operation. A typical charge/discharge curves is shown in Fig 3. By first a charge and discharge the depth and utilization of material of the electrolyte solution (by iron) were 73.7% and 48% respectively.

2) Coulombic, Voltage and Energy Efficiencies of the Cell

Through the continued charge/discharge 24 cycles values for the parameters obtained were showed in Table 1. It is clear that this cell has 73% average energy efficiency, 93% average coulombic efficiency and 78% average voltage efficiency.

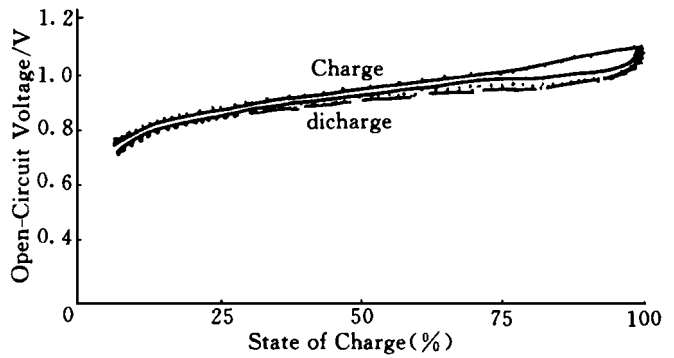


Fig 2 Open-circuit voltage behaviour of the cell at 25 ± 0.2 charging current 34 mA/cm^2 curves: — first cycle --- tenth cycle - · - · twentieth cycle

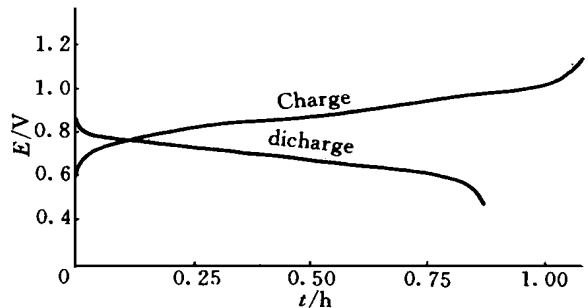


Fig 3 Charge/discharge curves of Fe-HP cell 22 ± 0.2 charge/discharge current 40 mA/cm^2

Tab 1 Efficiencies of the Cell

charge/discharge cycle	1	2	4	6	8	10	12	14	16	18	20	22	24
η_c (%)	93.00	92.96	93.58	93.75	94.00	93.50	93.30	93.44	92.97	92.88	93.46	93.26	92.94
η_v (%)	78.98	78.65	78.72	78.64	78.73	78.77	78.74	78.58	78.85	78.77	78.16	77.89	78.43
η_e (%)	73.45	73.11	73.67	73.80	73.92	73.64	73.21	73.42	73.31	73.16	73.05	72.64	72.89

3) Study of the Behaviour of the Cell at Several Heteropolyacids(HP)

a Variation of the Internal Resistance for the Cell

During the first cycle, the polarization curves in charge and discharge at 50% the state-of-charge have been obtained. Cell resistances were measured from the slopes of the charge and discharge polarization curves (Tab. 2).

b Variation of Efficiencies of the Cell

Coulombic, voltage and energy efficiencies have been obtained at different HP, average values for the parameters obtained in each are compared (Tab. 2).

Tab. 2 Experimental Data of the Cell at Different HP

HP	R_c^a	R_d^b	η_c	η_v	η_E
PMO ₁₂	4.2	4.3	93	78	73
PW ₁₂	5.0	5.1	84	75	63
SMO ₁₂	5.3	5.5	82	73	60
SW ₁₂	5.6	5.7	80	71	57

R_c^a and R_d^b : Charge and discharge resistance (Ωm^2)

η_c , η_v and η_E : coulombic, voltage and energy efficiencies (%)

PMO₁₂, PW₁₂, SMO₁₂ and SW₁₂: H₃PMO₁₂O₄₀, H₃PW₁₂O₄₀, H₄SMO₁₂O₄₀ and H₄SW₁₂O₄₀

Table 2 shows the best results were achieved with H₃PMO₁₂O₄₀. Electrochemical behaviour of heteropolyacid have been investigated^[11]. The study shows that the heteropolyacid has well redox reversibility.

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