ZETA POTENTIAL AT SULPHURIC ACID-BATTERY SEPARATOR INTERFACE

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Electrokinetic zeta potential of commercial battery separators has been determined using streaming potential measurements. The effect of pore size and other pore properties in conjunction with zeta potential on electrical resistance of battery separators is brought out from experimental data. Zeta potential effects with high positive charge accumulation affect the electrical resistance of submicroporous separators.

Key words: Zeta potential, battery separator, streaming potential measurement

INTRODUCTION

The effective functioning of battery separator depends on the free diffusion of electrolyte through it to the reaction site. The permeation is controlled by the porosity, pore size, distribution of pores, and tortuosity. However, the significance of electrokinetic effects due to charge separation at the separator-electrolyte interface has not been recognised fully [1]. A porous separator is in effect an assembly of a mass of capillaries with irregular packing. Diffusion of charged electrolyte and other ionic species (like Sb^V, Sb^{III}, or Pb^{II} etc) through the pores have to undergo the influence of the zeta potential at the interface. Such a potential may impede or aid the passage of the species across the separator. Since the reaction rate is controlled by diffusion of the species to the plates, the performance of the battery is very much influenced, especially at high discharge rates and at low temperatures.

Measurement of streaming or electro-osmotic potential can throw light on such behaviour [2]. Very few investigations of this type have been made on commercial separators [3]. Electrokinetic potential depends on the nature of material, nature and concentration of leachable ionic species in separator, adsorption characteristics, viscosity, and dielectric constant at the interface. With a variety of polymeric and other materials such as PVC, polypropylene, glass, rubber,etc. , being used especially with submicro pores, such effects are prominent and vary from type to type.

Herein a report on the electrokinetic behaviour of Indian separators is presented for the first time. In the present study, the streaming potentials at water-separator and electrolyte-separator interface have been experimentally determined. A comparative analysis and interplay of the various properties like porosity, pore size, tortuosity, electrical resistance and zeta potential is made to elucidate the functioning of the separator in the battery.

EXPERIMENTAL

All glass, polyethylene (both imported), rubber (five types) and PVC (seven types) separators have been studied. Distilled water and H_2SO_4 (1.28 sp.gr) are used as the fluids. The cell used for the measurement of streaming potential is made of perspex blocks as shown in Fig.1.
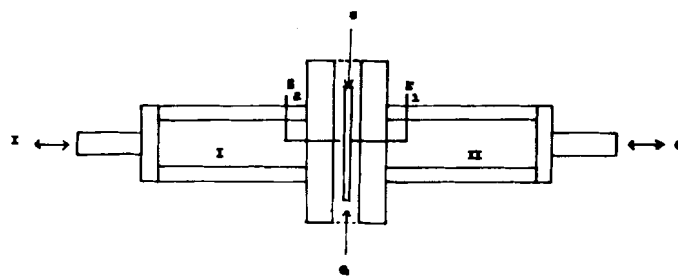

Fig. 1: Schematic diagram of the cell used for streaming potential measurements: S is the separator; E_1 and E_2 are the platinum electrodes; I is the fluid inlet whereas O is the outlet; G is the rubber gasket

The cell is similar to the one reported earlier [3]. The two halves of the cell I and II are assembled together with the separator positioned at the junction with gaskets to avoid leakage of electrolyte. Two platinum wire electrodes E_1 and E_2 are used here for monitoring the streaming potential ---E_1 connected to the positive of the digital voltmeter and E_2 to negative. The fluid flow was maintained by a constant pressure head reservoir. The flow was directed from flat side of separator to the ribbed side. All experiments were carried out at 303K.

Electrical resistance of separators is measured using Autobas[4] and the other properties as prescribed by IS-6071 [5].

RESULTS AND DISCUSSION

Streaming potential is related to the zeta potential by the following relation

$$S = \frac{\zeta D P}{4\pi \eta k_c}$$

where
ζ = Zeta potential
D = Dielectric constant of the double layer (assumed as 80)
P = Pressure head (dynes/cm²)
η = Viscosity coefficient of fluid (poise)
k_c = Specific conductance of fluid (ohm-cm) at interface

TABLE-I: Properties of all glass, polyethylene and rubber separators

Properties	All glass	Polyethylene	Microporous rubber	Rubber			
				1	2	3	4
Predominant pore size (μm)	38.00	1.20	4.00	1.70	1.60	1.80	1.60
Porosity (%)	85.00	75.00	66.00	60.00	63.00	60.00	59.00
Tortuosity	1.23	1.58	1.20	1.26	1.45	1.35	1.37
Electrical resistance (ohm-cm)	1.00	3.00	1.50	2.60	3.00	2.60	2.80
Streaming potential in water (V)	-0.06	-0.05	-0.10	-0.09	-0.12	-0.1	-0.12
Streaming potential in 1.28 sp.gr sulphuric acid (V)	+0.10	+0.25	-0.02	-0.04	+0.03	-0.001	+0.24
Zeta potential in water (10^{-14}V)	-0.17	-0.15	-0.28	-0.28	-0.35	-0.28	-0.30
Zeta potential in 1.28 sp.gr. sulphuric acid (10^{-8}V)	+1.24	+1.97	-0.18	-0.33	+0.25	-0.01	+1.86
Flow rate of sulphuric acid ($ml.s^{-1}$)	4.00	0.03	0.02	0.06	0.003	0.03	0.08

TABLE-II: Properties of PVC separators

Properties	PVC SAMPLES							
	1	2	3	4	5	6	7	8
Predominant pore size (μm)	15.1	56.5	21.2	33.9	32.0	38.0	27.1	30.8
Porosity (%)	50.0	57	60	41	52	48	52	49
Tortuosity	1.38	1.50	1.33	1.10	1.27	1.49	1.70	1.24
Electrical resistance (ohm-cm)	3.60	3.80	2.50	2.50	2.70	4.70	5.90	2.70
Streaming potential in water (V)	-0.17	-0.14	-0.15	-0.03	-0.04	-0.06	-0.09	-0.07
Streaming potential in 1.28 sp.gr. sulphuric acid (V)	+0.03	+0.08	-0.02	+0.10	+0.19	-0.03	-0.04	-0.04
Zeta potential in water (10^{-14}V)	-1.40	-1.03	-1.79	-0.31	-0.46	-0.38	-0.44	-0.77
Zeta potential in 1.28 sp. gr. sulphuric acid (10^{-8}V)	+0.05	+1.42	-0.39	+0.03	+4.60	-0.45	-0.43	-0.88
Flow rate of sulphuric acid (ml. s^{-1})	2.0	5.3	3.0	2.0	1.3	1.5	1.5	1.5

Zeta potential is calculated from the experimental streaming potential value and using known values of other terms in the equation. The results are presented in Tables I and II. Table I gives the values for glass, polyethylene and five types of rubber separators. Table II gives the results for 8 types of PVC separators. The values in water medium and in H_2SO_4 (sp.gr 1.28) are presented. The Table also includes the results of experimental values of pore size, porosity, tortuosity, electrical resistance, and flow rate of liquid in the cell under streaming potential conditions.

The streaming potential values for all types of separators studied in distilled water have negative values indicating fixed part of the double layer having negative ions and the diffusion layer positive ions. Some of the PVC separators show higher charge separation features probably because of chloride ions. One type of rubber separator also has this feature probably due to incorporation of some ionising material used in compounding.

The studies in H_2SO_4 (sp.gr 1.28) reveal interesting features. It is to be expected that higher concentration of hydrogen ions can alter the nature of the double layer. In many cases the potential shifts from negative to moderately positive or high positive values indicating a change in fixed and diffuse double layer structures. Such an effect can have influence on the diffusion of ions through the pores.

The data from Table I shows that when the pore size and porosity are very high (e.g. all glass), the charge separation has no significant effect. The electrical resistance is found to be low though high positive charge accumulation at the interface can impede the diffusion of positive ions through pores (as the fluid flow direction is from flat side of separator to rib side). This is evidenced by its high resistance in the case of polyethylene separator. The fine sub-micro pores and high positive charge accumulation have significant contribution for ion transport resulting in the higher resistance.

Separators with a negative zeta potential of very low positive values may not impede the flow of positive ions. Microporous rubber separators are predominantly of this type.

In the case of PVC separators (Table II), it is seen that the predominant nature is one of negative or very low positive zeta potential. This situation is favourable for the diffusion of positive ions and good performance of battery. In these types of separators, the porosity is comparatively low. However as the pore size is significant, even very high positive zeta potential may not be harmful (cf. sample 5). But the facts like blind pores or high tortuosity can cause higher electrical resistance (cf.sample 7) even if the zeta potential is favourable.

The flow rate values are dependent on both pore size and zeta potential as can clearly be seen in rubber separators.

CONCLUSION

From the study, it is seen that zeta potential at the pore interface varies in magnitude and sign from type to type and in the same type depending on the nature of material, processing condition and presence of addition agents. The zeta potential effect is significant when the pore size becomes significantly low to be comparable to double layer dimensions. When pore size is very large, the zeta potential may not influence performance of separators. In a battery under varying stages of discharge, especially under high rate conditions, the electrolyte concentration keeps varying, and it becomes essential to establish the variation of zeta potential under such behaviour. The performance of a separator will be dependent on the electrical resistance as well as the diffusion of hydrogen ions especially to positive plates. At high discharge rates the role of diffusion and zeta potential may take predominance.

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