ZETA POTENTIAL AT WATER-BATTERY SEPARATORS INTERFACE

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Zeta-potential at the interface of water and some battery separators is reported by using streaming potential experiments. Results are discussed briefly in terms of the charge density at the interface and its role in the battery performance.

Each electrochemical device for an alternate energy source involves a separator and performance the batteries has been attributed largely to the proper functioning of the separators [1]. During operation of these devices, the electrolyte components move from one electrode compartment to another through the separators. This flow depends on the selective characteristics of the separators arising from porosity, the hydrophilic or hydrophobic character, and the charge density at the liquid-separator interface. In the present study, the porosity of different separators and zeta-potential at water-separator interface is determined from the streaming potential measurements.

EXPERIMENTAL

Material

Deionised water having specific conductance of the order of 10^{-6} ohm^{-1} cm^{-1} was used for the study.

Ion exchange separator Zamm-O supplied by RAI-millipore Co., New York; polysulphone HT-100 and HT-200 supplied by Gelamn Sciences Inc., Ann Arbor, MI, U.S.A.; Cellgard 3400, K 1685P on PP S49024 and WR Grace interseparator supplied supplied by Grace Company, New York, were used.

Bright platinum foil having small holes for free flow of water during streaming was used as the electrodes.

Procedure

All plexiglass cell was constructed for the measurement of the streaming potential in the present investigation. The cell consists of two plexiglass blocks I and II each having dimensions 3" x 3" x $1\frac{1}{2}$". Each block has void volume of 1.C $inch^3$ with an opening of 1" diameter on one side of the block. Two stainless steel 1/4" fittings S_1 and S_2 were attached to the top of the each block for the insertion of the electrodes and two other fittings S_3 and S_4 on the sides for the inlet and outlet of water during streaming. The separator, M, was placed between the hollow space in the blocks. The apparatus is shown in Fig.1. To ensure that the apparatus does not leak, a rubber O-ring was used on one side of the block facing the separator.

The liquid was flown through the separator at constant pressure difference. The pressure difference was maintained either by nitrogen gas (Fig.1a) or by a water reservoir (Fig.1b). If the flow is fast, the water reservoir is used. Otherwise nitrogen gas from a compressed cylinder was used for the streaming of the liquid. The presseure is maintained constant either with a overflowing reservoir or with a needle value, V. The nitrogen gas pressure difference across the separator was read in the pressure gauge, P The error in the

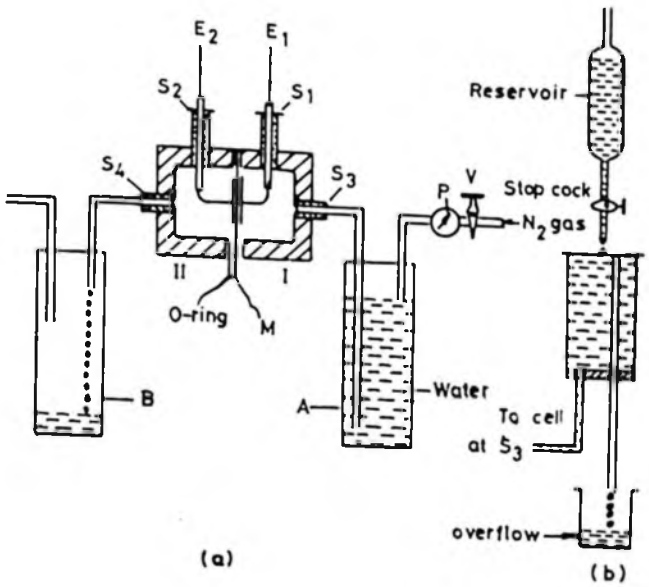


Fig. 1 Streaming Potential Apparatus

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pressure gauge at the reading of 3.0 p.s.i is 2%. The streaming potential developed across the separator is measured through electrodes E_1 and E_2 by 616 Keithley digital electrometer. The resistance of the system was also measured with the electrometer and the specific conductance of water was measured with the solution, analyzer no.4503A supplied by Amber Science Co., San Diego, U.S.A. The permeability coefficient, L_{22} required in the estimation of Zeta-potential was measured by the usual procedure [1]. All experiments were carried out at room temperature i.e. 25 ± 0.5° C. The streaming potential at different values of pressure difference were determined for the battery separators.

RESULTS AND DISCUSSION

Number of theories to explain the effect of streaming potential have appeared in the literature [2,3]. Overbeck [4] gave a thermodynamic theory based on the concepts of non-equilibrium thermodynamics [5,6]. This theory has the advantage that it does not assume any model and holds good near equilibrium conditions. In such effects there is a simultaneous transport of matter and electricity through the separators.

The rate of permeation through a separator under the simultaneous influence of a gradient of the hydrostatic pressure and an electric field dpends on the effective cross-section, A and the thickness of the separator, l : An unambiguous determination of either of these quantities is difficult due to the complex geometry of the openings within the separator. It is, however, possible to determine the ratio A/l, the so called separator constant [7], in terms of which the permeation behaviour of any separator can be expressed quantitatively.

For a separator having n pores of equivalent radius, r the effective cross-sectional area, A through which permeation occurs is $n \pi r^2$. The electrical conductace, K. of the separator equillibrated with a permeant having specific conductance, k is given [7] by

$$K = \frac{n \pi r^2 k}{l} = \frac{A}{l} \cdot k \qquad (1)$$

so that the membrane constant is equal to

$$\frac{A}{l} = \frac{K}{k} \qquad (2)$$

This constant, A/l is a characteristic quantity of the separator and is independant of the nature of the permeating liquid-atleast as long as the interaction between the permeant and the membrane matrix is not strong enough to alter its equivalent pore radius. Membrane charactristics for the different separators are given in Table 1.

According to the theory of thermodyamics of irreversible processes [5], the streaming potential, $\Delta \varphi_s$ is defined as the potential difference divided by pressure difference, ΔP in the state with zero electric current, I and is expreseed as:

$$\left[\frac{\Delta \varphi_s}{\Delta P}\right]_{I=0} = -\frac{L_{12}}{L_{11}} \qquad (3)$$

where L_{11} and L_{12} are the phenomenological coefficients. L_{11} is the electrical conductance and is reciprocal of the resistance, R, of the streaming potential cell (subsystems + separator). Accordingly equation (3) becomes

$$\left[\frac{\Delta \varphi_s}{\Delta P}\right]_{I=0} = L_{12} \cdot R \qquad (4)$$

TABLE 1

DIMENSIONAL CHARACTERISTICS OF DIFFERENT SEPARATORS

Separator	K x 10^6 (Ω^{-1})	k x 10^4 ($\Omega^{-1}m^{-1}$)	A/l x 10^3 (m)
1. Polysulphore, HT-100	1.010	1.08	9.35
	1.037		9.60
	1.019		9.44
	0.994		9.20
2. Celgard 3400	0.831	1.08	7.70
3. Polysulphone, HT-200	0.476	1.08	4.41
4. K 1865p on pp 49024	3.444	1.08	30.97
5. Ion Exchange (Zamm-0)	2.475	1.08	22.92
6. WR Grace Inter-separator	3.953	1.08	36.60

L_{12} is also called electro-osmotic permeability coefficient and it is estimated from the linear plots of $\Delta\varphi_s$ versus ΔP. These values are given in Table 2 along with other data.

The electrical conductance, L_{11} and the permeability coefficient, L_{22} can be written [7] as

$$L_{11} = \frac{n \pi r^2 . k}{l} \qquad (5)$$

and

$$L_{22} = \frac{n \pi r^4}{8 \eta l} \qquad (6)$$

where η is the coefficient of viscosity of the liquid. From equation (5) and (6), it follows easily that

$$r = \left[\frac{8 \eta K . L_{22}}{L_{11}}\right]^{1/2} \qquad (7)$$

Substituting the values of η , k , L_{22} , L_{11} , the equivalent pore radius r can be estimated from equation (7). Here the values of L_{22} and L_{11} per unit area of the separator have been used. Knowing r, we get the number of pores of the separator surface from equation (6) as

$$n = \frac{8 \eta l . L_{22}}{\pi r^4} \qquad (8)$$

n per unit area of the separator is given by

$$n = \frac{8 \eta l L_{22}}{r^4} . R'^2$$

where R' is the radius of the separator used. The values of the pore radius and the number of pores in the separator are given in Table 2

The electrical character of a separator-liquid interface can be expressed in terms of the zeta-potential ζ where r is much larger than the double layer thickness. According to the double-layer picture [8], the electro-osmotic permeability, is given by

$$L_{12} = \frac{n \varepsilon r^2 \zeta}{4 \eta l} \qquad (9)$$

TABLE 2

PHENOMENOLOGICAL CHARACTERISTICS OF THE SEPARATORS

Separator	Thickness mm	$L_{11} \times 10^6$ (Ω^{-1})	L_{22} ($m^3 s^{-1} N^{-1}$)	$L_{12} \times 10^{12}$ ($m^3 A J^{-1}$)	r micron	n	ζ (μV)
1. Polysulphone (HT-100)	0.1	1.010		1.055	1.22	1.99×10^5	0.162
		1.037		1.054	1.23	1.93×10^5	0.164
		1.019	0.0384×10^{-7}	1.006	1.21	2.06×10^5	0.152
		0.994		1.001	1.23	1.93×10^5	0.156
2. Cellagard(3400)	0.025	0.8313	1.539×10^{-13}	0.5187	8.49×10^{-3}	8.50×10^8	0.096
3. Polysulphone	0.15	0.4762	0.0856×10^{-7}	0.8983	2.65	2.99×10^4	0.292
4. K 1685P on PPS 49024	0.313	3.344	2.496×10^{-9}	42.22	0.539	1.06×10^7	1.95
5. Ion Exchange (Zamm-O)	0.313	2.475	1.156×10^{-12}	28.67	1.35×10^{-2}	1.25×10^9	1.79
6. WR Grace Interseparator	0.169	3.953	0.647×10^{-7}	52.45	2.53	3.06×10^5	2.06

or

$$\zeta = \frac{4\eta l . L_{22}}{h r^2 \varepsilon} \qquad (10)$$

where ε is the bulk dielectric constant of the liquid. The values of different characteristic viz., L_{11}, L_{12}, L_{22}, r, n and zeta-potential are given Table 2. The values of the ζ potential of different separators suggests that the surface charge density is much higher in case of WR Grace interseparator, Zamm-O and K on PP separators. Greater charge density indicates the possibility of greater electrostatic interaction between the liquid and the separator material. This greater interaction further suggests that the flow through these separators is indicative of extensive ordering process in comparison to other separators studied here. It has been observed that separators in certain batteries dry out during cycling and it may be attributed to lesser interactions between the liquid and the separator material. In view of the present values of zeta-potential, it can be inferred that the dyring of the battery separators during cycling and hence the performance of the battery can be improved if these separators (WR Grace interseparator, ion exchange (Zamm-O) and K on PP) are used alone or in combination in series with each other in the battery.

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