

Surface charge and function of cellulose battery separators

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Received 8 January

The results of zeta-potential determination using the electro-osmotic method in dilute (10^{-3} mol dm $^{-3}$) solutions of NH $_4$ Cl and ZnCl $_2$ and diffusion parameters measured in 20% NH $_4$ Cl and 30% ZnCl $_2$ solutions are presented. In both cases cellulosic membrane separators from different manufacturers, already in practical usage in Leclanché cells, were examined. From the measured data, diffusion potentials were calculated and compared with experimental values. Transport numbers calculated from diffusion potentials are compared to values in free solution (i.e. without a membrane). The relevance of these parameters to the role of cellulosic separators in Leclanché-type cells is briefly discussed.

1. Introduction

During deep discharge of the Leclanché cell the water which is transferred from the cathodic to the anodic region may penetrate the cell wall and leak out.

According to theoretical considerations the separator could have an influence upon this phenomenon. The aim of this work is to examine a specific approach to the role of cellulose separators, especially in Leclanché or similar cells.

It has been established [1, 2] that the cellulose carries a negative surface charge and therefore the cellulose separator acts selectively on ion diffusion, slowing down ions of the same sign and speeding up those of the opposite sign. Moreover electro-osmotic transport of water can take place through the separator. If a certain ionic species accumulates in one electrode region because of its slower diffusion, the osmotic transport of water tends to equalize the chemical potentials.

These two phenomena might proceed in the same direction and the transport of water would then be greater. In order to explain certain phenomena during the period of discharge and

between discharges, investigations of electro-osmotic transport and ion diffusion through separators were performed. Various types of commercial separators from different manufacturers were investigated and designated simply as A, B, C, D and E. Their characteristics are shown in Table 1.

2. Experimental procedure

2.1. Electro-osmosis

The measurement of the electro-osmotic flow in 10^{-3} mol dm $^{-3}$ solutions of NH $_4$ Cl and in 5×10^{-3} mol dm $^{-3}$ solutions of ZnCl $_2$ was carried

Table 1. Separator characteristics

Separator	Paper (g m $^{-2}$)	Gel coating (g m $^{-2}$)	Manufacturer
A	90	30-35	Aero, Yugoslavia
B	60-70	35-40	Matsushita, Japan
C	50-60	35-40	Jointine, England
D	90	30-35	Vidor, England
E	70	40	Varta, Germany

Table 2. Zeta-potential (mV) for separators A and B

Solution	A	B
NH ₄ Cl (10 ⁻³ mol dm ⁻³)	-0.1	-0.1
ZnCl ₂ (5 × 10 ⁻³ mol dm ⁻³)	-0.3	-0.6

out on apparatus which has been described elsewhere [3]. Two types of commercial separators, A and B, were used as membranes.

From the given volume transport of the examined solution V , and using the data for dynamic viscosity of the solution η , specific conductivity κ , dielectric constant ϵ , electric current I , the zeta-potential ζ was calculated according to Smoluchowski's equation

$$\zeta = 3.6 \times 10^5 V \pi \eta \kappa / I \epsilon. \quad (1)$$

The values of zeta-potential with both solutions for separators A and B are shown in the Table 2.

2.2. Ionic diffusion

As the experimental equipment and procedure have already been described in another paper [3], they will not be discussed here.

Measurement was begun at the moment when both half cells were filled with liquid: the left one with a 20% solution of NH₄Cl, or a 30% solution of ZnCl₂, the right one with distilled water. A membrane separator is placed between the half cells. Because of the concentration gradient, diffusion of ions occurs from the more concentrated into the dilute solution (i.e. water). Immersed electrodes, two calomel, one glass and a Ag/AgCl electrode were used to follow the diffusion of Cl⁻ and H⁺ ions at the same time as following the potential difference.

2.3. Activities of the H⁺ and Cl⁻ ions

The change of Cl⁻ and H⁺ ion activity with time was determined by measuring the Ag/AgCl electrode potential and the solution pH. The activity of the Cl⁻ ions was calculated from the following equation

$$\log a_{\text{Cl}^-} = (E - 0.0216)/0.059 \quad (2)$$

where E represents the emf of the cell

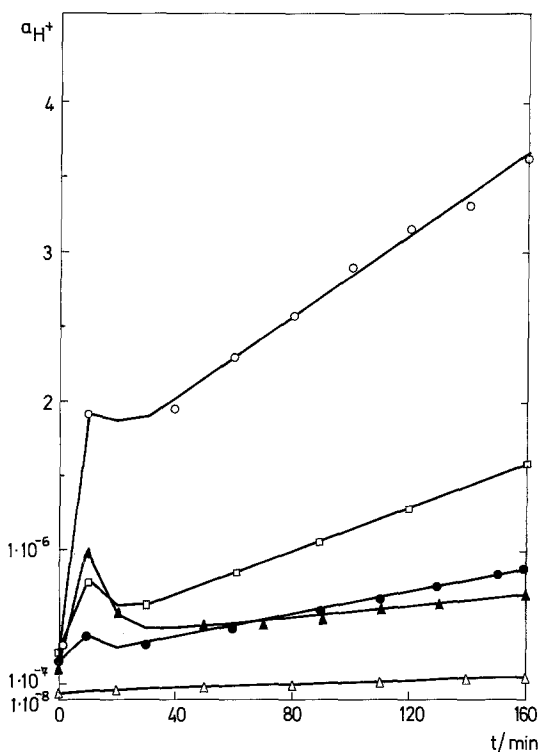


Fig. 1. Changes in the activity of H⁺ ions with time in 20% NH₄Cl solution through separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E.

$E_{\text{SCE}}/E_{\text{Ag, AgCl}}$. Characteristic measurements of H⁺ ion activity in solutions of 20% NH₄Cl and 30% ZnCl₂ are shown in Figs. 1 and 2. At the beginning there is a period of instability, the change of activity is rapid and there is a linear increase in the NH₄Cl solution, while in the ZnCl₂ solution there is a nonlinear decrease (except for separator B). For the linear range in the NH₄Cl solution (after 50 min), a correlation analysis was carried out for the measured values for an interval of 50–170 min. The results are shown in Fig. 3, and represent average values of six measurements for separators A, B, C, D and E.

Changes of Cl⁻ ion activity in the NH₄Cl and ZnCl₂ solutions for all five types of separator are shown in Figs. 4 and 5.

3. Discussion

The flux* of Cl⁻ ions has been calculated from the slope of the straight line plot of Cl⁻ ion activity

* see Derniković *et al.* [3].

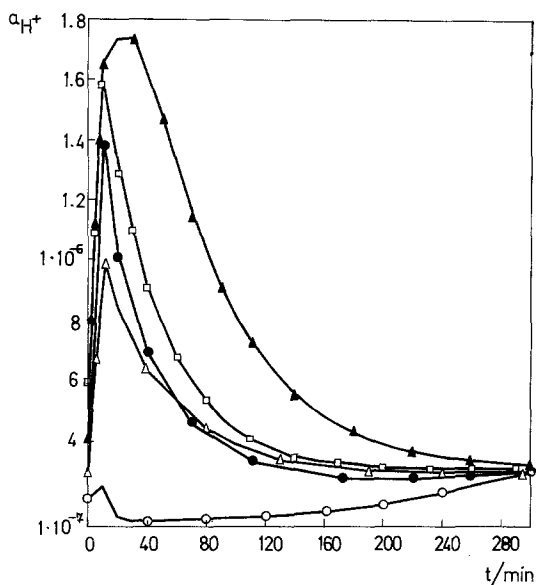


Fig. 2. Changes in the activity of H⁺ ions with time in 30% ZnCl₂ solution through separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E.

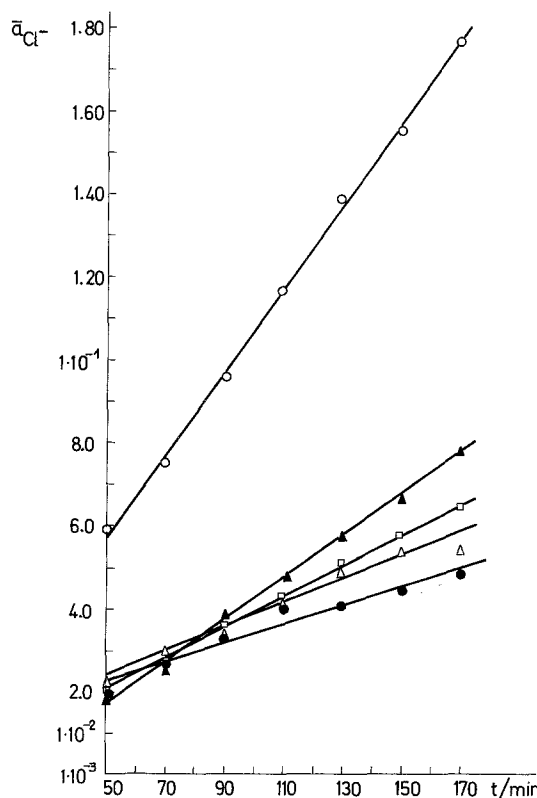


Fig. 4. Changes in the activity of Cl⁻ ions with time in 20% NH₄Cl solution through separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E.

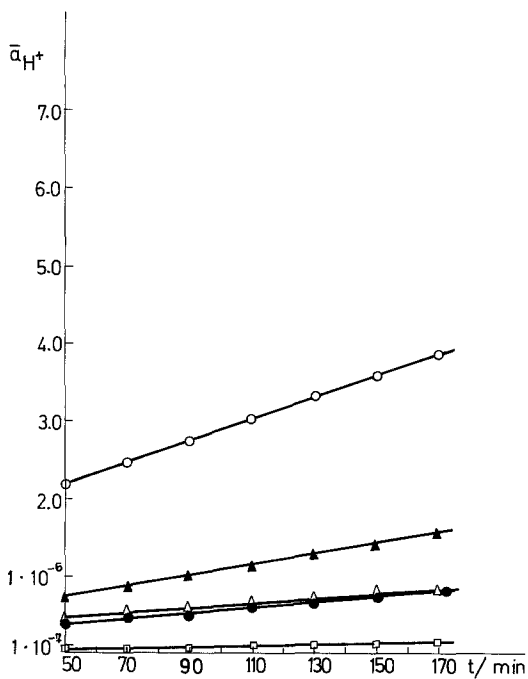


Fig. 3. Changes in the activity of H⁺ ions with time in 20% NH₄Cl solution through separators A, B, C, D and E (result obtained by correlation analysis). ●, A; ○, B; ▲, C; □, D; △, E.

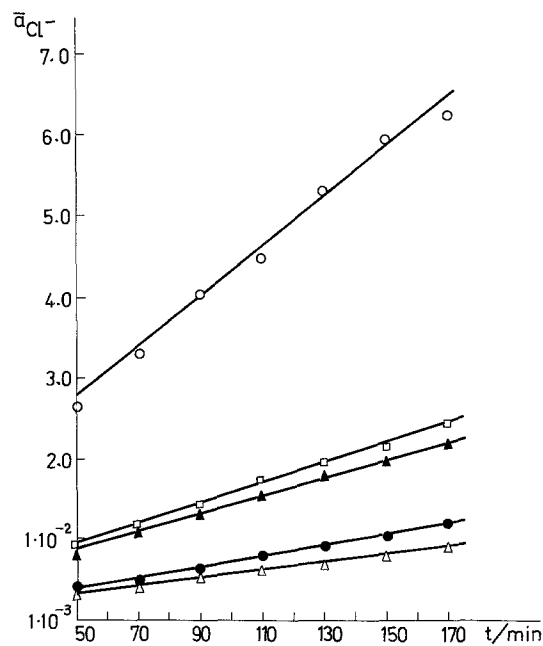


Fig. 5. Changes in the activity of Cl⁻ ions with time in 30% ZnCl₂ solution through separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E.

Table 3. Flux of Cl^- ions in 20% NH_4Cl solution

Separator	Flux ($\mu\text{mol cm}^{-2} \text{min}^{-1}$)
A	21.5
B	93.7
C	27.0
D	47.7
E	34.3

change with time (Tables 3 and 4). H^+ ion flux has not been determined, because values of the same order can be obtained from salt hydrolysis. Moreover the H^+ ion activity change in ZnCl_2 solution is nonlinear, so that the flux is not constant. Activities and equivalent conductivities of ions have been used for the calculation of diffusion potentials according to Henderson's equation

$$E_{\text{diff}} = -\frac{RT}{F} \frac{\sum \frac{\lambda_i}{z_i} (C_i^{\text{II}} - C_i^{\text{I}})}{\sum \lambda_i (C_i^{\text{II}} - C_i^{\text{I}})} \ln \frac{\sum \lambda_i C_i^{\text{II}}}{\sum \lambda_i C_i^{\text{I}}} \quad (3)$$

where C_i^{I} and C_i^{II} represent the molar ionic con-

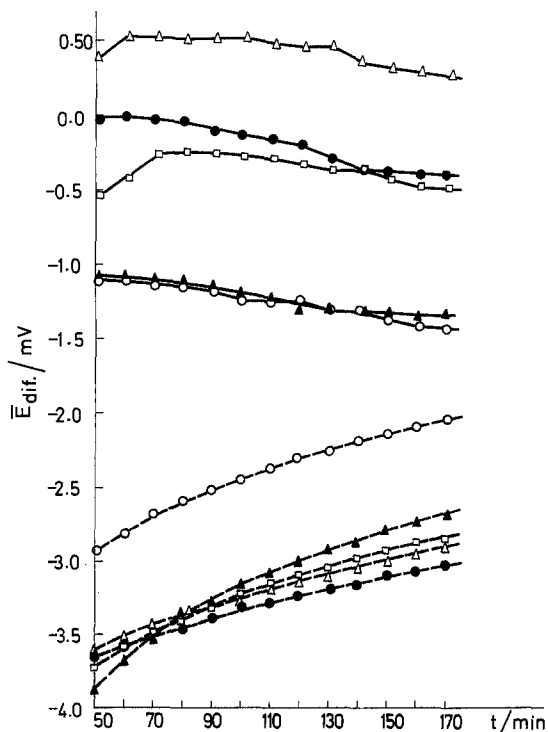


Fig. 6. Changes in the diffusion potentials with time in 20% NH_4Cl solution through separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E. — measured values, - - - - calculated values.

Table 4. Flux of Cl^- ions in 30% ZnCl_2 solution

Separator	Flux ($\mu\text{mol cm}^{-2} \text{min}^{-1}$)
A	6.21
B	29.10
C	4.51
D	10.80
E	11.60

centrations present in solutions II (more concentrated) and I (more diluted), respectively, and λ_i is the equivalent ionic conductivity depending on the solution concentration.

A comparison of measured and calculated values (Figs. 6 and 7) points to the existence of a surface electric charge on the membrane.

Transport numbers also show the selective effect of the membrane, i.e., retardation of diffusion of ions of the same sign and acceleration as those of opposite charge. Apparent transport numbers of cations were calculated according to the equation

$$t^+ = 1/2 \left(1 + \frac{E_{\text{diff}}}{0.059 \log a^{\text{I}}/a^{\text{II}}} \right) \quad (4)$$

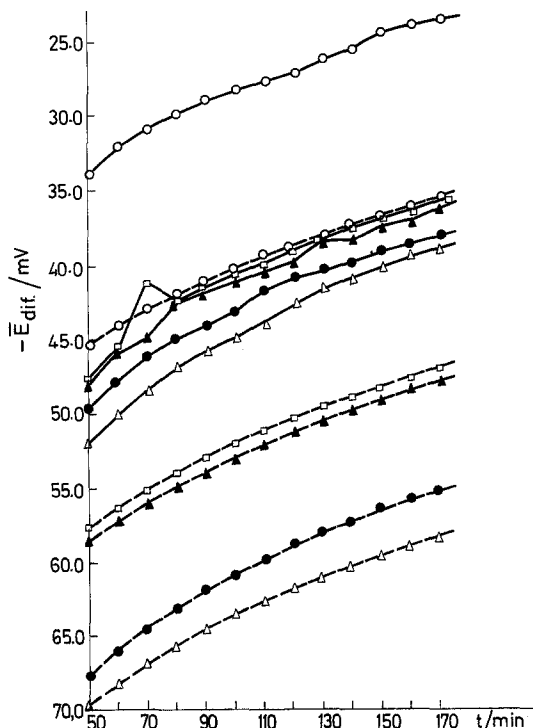


Fig. 7. Changes in the diffusion potentials with time in 30% ZnCl_2 solution through separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E. — measured values, - - - - calculated values.

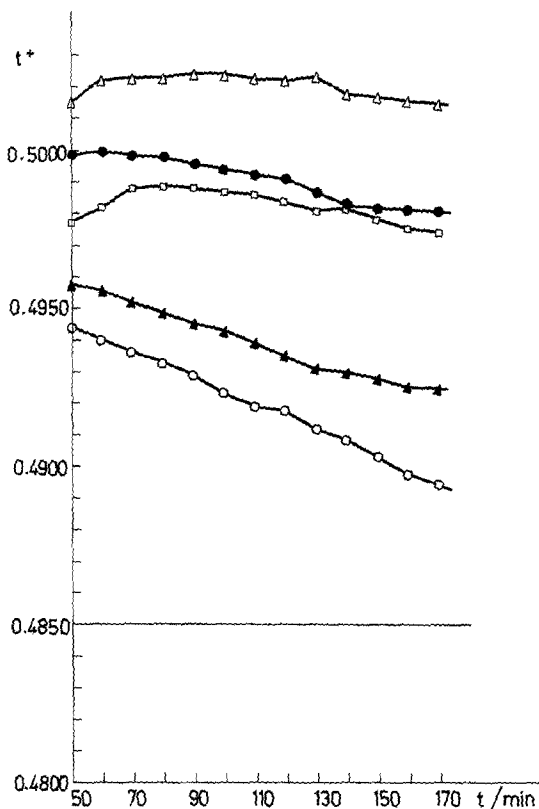


Fig. 8. Transport number of cations in 20% NH_4Cl solution with separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E. Value of t^+ in the solution without separators 0.4850.

for the NH_4Cl solution and

$$t^+ = 2/3 \left(1 + \frac{E_{\text{diff}}}{0.059 \log a^{\text{I}}/a^{\text{II}}} \right) \quad (5)$$

for the ZnCl_2 solution. The results are shown in Figs. 8 and 9, which also show the transport numbers in free solutions of the same concentration, (data from the literature [4]), so that it is possible to evaluate directly the effect of the membrane on the ionic diffusion.

The results obtained can be compared with those for NH_4Cl and ZnCl_2 solutions, but it is interesting to consider the measured values for the separators and papers (used as a basis in the production of separators) in order to examine the influence of the gelatinous coating. The measurements for papers have already been given in another paper [3] and will be used here for discussion. Flux of Cl^- ions is higher in a 30% solution of ZnCl_2 than in 20% solution of NH_4Cl

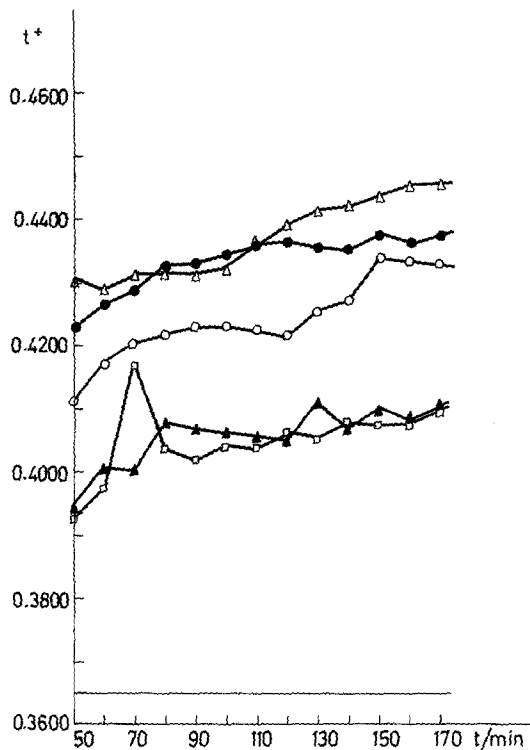


Fig. 9. Transport number of cations in 30% ZnCl_2 solution with separators A, B, C, D and E. ●, A; ○, B; ▲, C; □, D; △, E. Value of t^+ in the solution without separators 0.3650.

(Tables 2 and 3) in all types of separator because of the larger concentration gradient in the ZnCl_2 solution. In order to compare these values for the separator and the paper only two-layered papers should be considered, because the separators have been protected by one layer of paper, so that the gelatinous coating does not come off their surface.

Such a comparison is possible only with types A and E (because only for A and E were two layered papers investigated), and it shows that the flux across the papers is higher than through the separators. In the ZnCl_2 solution the diffusion potentials in the separators are 30–50 times higher than in NH_4Cl solution. Comparison of these values for the separators and the papers is also only possible for types A and E. In the NH_4Cl solution the potentials have slightly more positive values with separators, and in the ZnCl_2 solution with papers.

Cation transport numbers for separators have larger values in the NH_4Cl solution (0.49–0.50) than in the ZnCl_2 solution (0.39–0.43). In both

solutions the transport numbers are larger with separators than with papers.

4. Conclusions

4.1. Summary

The cation transport numbers for the same membrane have higher values in a NH_4Cl solution than in a ZnCl_2 solution because of the greater mobility of NH_4^+ ions. The cation transport numbers are higher in a membrane system (especially with a separator) than in a free solution and they indicate that the membrane carries a surface charge which acts selectively on the ionic transport rate.

It is also concluded by comparison of separators and papers, that the gelatinous coating on the separator influences the surface charge of the cellulose membrane and makes the zeta-potential more positive, which is reflected in the membrane properties.

4.2. Application to batteries

These results, literature data and general observations on battery performance can now be combined to give some new ideas to explain processes inside a battery. The experimental measurements confirmed the expected transport of water towards the anode. When the cell discharges, more Zn^{2+} ions appear in the anode region. Zn^{2+} ion concentration increases with time because of their lower transport number compared with anions, although the negatively charged separator membrane accelerates the diffusion.

According to Schumm [5] the complexed, weakly soluble products of zinc formed with time slow down its diffusion from the anode. During the measurements it was observed that these salts also precipitate on the separator, filling its pores. The measured transport numbers of NH_4^+ ions are insignificantly lower than the transport numbers

of the anions (Cl^-), because of the acceleration from the negatively charged cellulose separator and the approximately equal mobilities of both ions. NH_4^+ ions diffuse into the cathode mix and their concentration in the anode region decreases with time according to Agopsowicz *et al.* [6]. They precipitate as complexes in the depolarizing mix. The separator influences ion diffusion in the period between the battery discharges. Maintenance of high zinc salt concentration in the anode region will cause the osmotic transport of water, which was observed in the more concentrated solution. When the cathode mix is exhausted, gas also appears and its pressure increases so much that water is pushed out of the cell and the battery leaks. The surfaces of the anode and separator become strongly acidic, the separator progressively deteriorates and the precipitated salts decrease the ion diffusion. As a consequence the cell performance deteriorates. From all of these considerations one can see that the reactions in a battery are very complicated and the separator functions are numerous, that is, it does not just play the role of mechanical separation between two parts of the cell.

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