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LIMITING CURRENTS AND SODIUM TRANSPORT NUMBERS IN NAFION MEMBRANES

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Abstract—An improved method to determine limiting currents I_L in cation exchange membranes based on the use of a microhole array attached onto the membrane surface is applied to the Nafion® 117 membrane in dilute aqueous NaCl solutions. The values for I_L obtained from the current–voltage curves are used to estimate the cation transport numbers t_1^s corresponding to the membrane operating under limiting current conditions. The changes of t_1^s with the NaCl concentration give some insights into the membrane selectivity, and cannot be described by the conventional Donnan theory for charged membranes. Instead, a two phase model accounting for different conductive phases in the membrane is able to describe the experimental trends.

Key words: Nafion® membrane, microhole array, limiting current conditions, cation transport numbers, membrane selectivity.

1. INTRODUCTION

In many electrically driven processes ion exchange membranes are employed close to the limiting current condition[1, 2] where their permselectivity differs significantly from the ideal behaviour. Therefore, when running such processes, knowledge of their actual selectivity is needed to analyze mass balances properly. Perfluorinated sulfonic acid membranes such as Nafion® (du Pont) have received much attention because of their unique selectivity properties. These properties can be characterized from, *eg* transport number measurements. Recently, Pak and Xu[3] have measured the proton transport number in Nafion membranes. They suggest that studies of different cations such as sodium could contribute to the understanding of the transport mechanisms in these membranes. We present here sodium transport number measurements in a Nafion 117 membrane under limiting current conditions, and give transport models which can describe the observed results.

According to the classical theory of concentration polarization (CP), the current–voltage (I–V) curve of an ideally selective ion exchange membrane should be linear for low applied voltages, then increase slowly, and finally reach a limiting value for the current density[4]. However, no true saturation is observed in practice. After passing through a region of slow variation, the current density continues to grow for high applied voltages. Furthermore, when employing, *eg* a rotating diffusion cell[4] the plateau region reduces to a single point of inflection and the value of the limiting current has to be obtained from indirect methods such as Cowan plots.

It is now accepted that the overlimiting currents of the cation exchange membranes are very likely related to electroconvective mixing of the depleted diffusion boundary layer (DBL)[5–9]. Although this point has sometimes been questioned[10], it is also agreed that the classical theory of CP can be used to obtain the value of the limiting current density[4–6, 9]. However, the permselectivity of the membrane has to be taken into account and the classical expression for the limiting current density has to be modified accordingly. This can be accomplished either in terms of the ratio of the ion fluxes[8, 11] or in terms of transport numbers[9]. The latter alternative brings the possibility of obtaining transport numbers from the observed values of the limiting current density.

In this paper we present an improved method of measuring the limiting current density and relate this measurement to the selectivity properties of the membrane. First, a filter with a microhole array is attached to the surface of the ion exchange membrane. On the one hand, this procedure reduces the convective mixing near the membrane and leads to I–V curves with a clearly defined plateau region. On the other hand, the filter allows for fixing the thickness of the depleted DBL which is a key parameter in the theory of CP. This thickness is not, unfortunately, directly accessible to measurement but it is to be evaluated from self-diffusion experiments[9]. Alternatively, different experimental setups with clearly defined thicknesses of the depleted DBL have been employed[4, 12, 13].

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Secondly, the measured values of the limiting currents at different bulk solution concentrations are employed to obtain the transport numbers of the Nafion 117 membrane at these concentrations. These transport numbers are related to the membrane selectivity under practical operation. Finally, it is shown that the conventional Donnan exclusion theory[14] cannot explain the experimental results, while a two phase model allowing for different conductive phases in the membrane gives a reasonable account of the results.

2. THEORY

The limiting current density can theoretically be obtained from the condition of zero ion concentration at the interface between the membrane and the depleted DBL[14, 15]. Ion transport through the DBL is usually described by the Nernst–Planck equations[14]

$$J_i = -D_i\left[\frac{dc_i}{dx} + (-1)^{i+1}c_i\frac{F}{RT}\frac{d\phi}{dx}\right] \quad i = 1, 2 \quad (1)$$

the condition of electroneutrality

$$c_1 = c_2 = c \quad (2)$$

and the equation for the electric current density

$$i = F(J_1 - J_2). \quad (3)$$

Here J_i, D_i and c_i denote the flux, diffusion coefficient and local molar concentration of the i-th species, respectively. Subscript 1 refers to the cation (counterion here, since Nafion 117 membrane is cation selective) and subscript 2 to the anion (coion). The electric potential is represented by ϕ, while F, R and T have their usual meanings. The combination of equations (1) and (2) gives an expression for the concentration gradient in the depleted DBL in terms of the ion fluxes:

$$\frac{dc}{dx} = -\frac{1}{2}\left(\frac{J_1}{D_1} + \frac{J_2}{D_2}\right). \quad (4)$$

If c^b denotes the bulk concentration at the outer boundary of the DBL, the concentration gradient which is attained under limiting current (i_L) conditions can be written as

$$\left(\frac{dc}{dx}\right)_{i_L} = -\frac{c^b}{\delta} = -\frac{1}{2}\left(\frac{J_1}{D_1} + \frac{J_2}{D_2}\right), \quad (5)$$

where δ denotes the thickness of the DBL. The use of equation (3) leads to the well known expression[15]

$$i_L = \frac{FDc^b}{(t_1^s - t_1^b)\delta}, \quad (6)$$

where $D \equiv 2D_1D_2/(D_1 + D_2)$ is the salt diffusion coefficient, $t_1^b \equiv D_1/(D_1 + D_2)$ is the transport number of the cation in the bulk solution, and

$$t_1^s \equiv \frac{J_1}{i/F} \quad (7)$$

is the transport number of the cation in the membrane system. It must be noted, however, that equation (6) is usually derived from the assumption that (back) diffusion can be neglected in the membrane (*ie* the transport is entirely migrational) and t_1^s then has the meaning of the transport number in the membrane[15].

Equation (6) must be appropriately modified to account for the characteristics of our experimental arrangement. In particular, the depleted DBL is here confined to the pores of the microhole array. Transport from the bulk solution to the membrane has to be divided into two parts: transport to the pore mouth, and then transport inside the pore (see Fig. 1). The former can be characterized by spherical diffusion while the latter is described by unidimensional equations like equation (1). Ion transport to the pore mouth is described by the generalization of equation (4) to the case of three dimensional transport:

$$\nabla c = -\frac{1}{2}\left(\frac{\vec{J}_1}{D_1} + \frac{\vec{J}_2}{D_2}\right) \quad (8)$$

which reduces to Laplace equation $\nabla^2 c = 0$ after making use of the steady-state continuity equations $\nabla\vec{J}_i = 0$, $i = 1, 2$. If r_0 is the pore radius and c_0 the concentration at the pore mouth, the solution of Laplace equation is given by

$$c(r) = c^b - (c^b - c_0)\frac{r_0}{r} \quad (9)$$

and then the condition of continuity for the ion flux and concentration leads to

$$c_0 = \frac{c^b}{1 + r_0/l} \quad (10)$$

where l is the pore length, *ie* the thickness of the filter. Therefore, the limiting current density is given by

$$i_L = \frac{FDc_0}{(t_1^s - t_1^b)l} = \frac{FDc^b}{(t_1^s - t_1^b)\delta}, \quad (11)$$

with $\delta = r_0 + l$ playing the role of an effective DBL thickness.

Equation (10) gives an estimate of the importance of the concentration polarization outside the pore. It

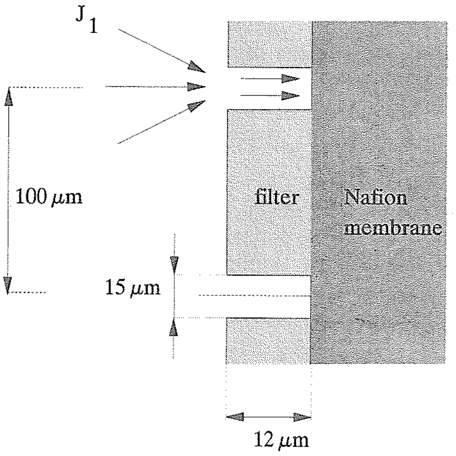

Fig. 1. A schematic view of the transport of cations to pore mouth and inside the pore. The relevant measures of the filter are also shown.

must be noticed that it is not an exact result since, strictly speaking, the diffusion to the pore mouth is not spherical. The particular distribution of the pores in the microarray should be taken into account and appropriate cells (with impermeable boundaries) should be considered. In fact, cylindrical geometry would yield more accurate results. However, it is not necessary to perform more sophisticated calculations, and the use of an effective pore radius $r'_0 \equiv 4r_0/\pi$ makes the error very small[16]. Still, equation (10) clearly shows that the correction for the CP outside the pore is important when l and r_0 (or r'_0) are of the same order of magnitude, as happens in our experiments. It should finally be mentioned that the microarray technique has previously been used in the study of the interface between two immiscible electrolyte solutions (ITIES)[17].

Equation (11) represents the limiting current density in the filter. This quantity is related to the observed limiting current I_L through the total pore area where transport is taking place. If A_g is the geometrical area of the microhole array exposed to current, and ε is the porosity of this filter, the limiting current can be written as

$$I_L = \frac{\varepsilon A_g F D c^b}{(t_1^s - t_1^b)\delta}. \qquad (12)$$

The current density in the Nafion membrane, with a porosity much higher than that of the filter, is much smaller than i_L in equation (11). Analogously, the current density in the enriched DBL is very small (when compared to i_L in equation (11)), and we can thus consider that there is no concentration polarization in the enriched DBL.

3. EXPERIMENTAL

The experimental setup for the measurement of the quasi-stationary state I–V curves is shown in Fig. 2. The measurements were carried out with a waveform generator (PP-RI HI-TEK Instruments) and a four terminal potentiostat built at the University of Southampton[18]. The cell was made of PTFE at the workshop of the Department of Chemistry, Helsinki University of Technology, and consisted of two compartments separated from each other with the filter and the cation exchange membrane. The area exposed was 0.031 cm^2 and the volume of the compartments was about 80 cm^3.

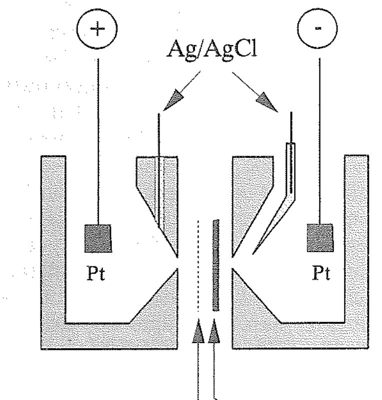

Fig. 2. Experimental setup for the measurement of the current–voltage curves.

The filter (a kind donation of Prof. Hubert Girault, University of Edinburgh) was prepared from a polyester film (Mylar, thickness 12 μm) by laser-drilling pores (diameter 15 μm) at the nodes of a regular hexagonal lattice with a lattice parameter of 100 μm (see Fig. 1). The side of the film in contact with the membrane was hydrophobic, while the other was hydrophilic. Thus, the close contact of the filter and the membrane is then assured. The membrane used was a Nafion 117 cation exchange membrane which contains no reinforcement net. Before the membrane was taken into use it was boiled in 3 wt.% H_2O_2 for 30 min, rinsed with hot water, kept for one hour in 0.5 M H_2SO_4 at 70°C, rinsed again with hot water and cleaned with ultrasonic.

Reference electrodes were prepared by electrolyzing AgCl on Ag wires in 0.1 M HCl with current density of 0.4 mA cm^{-2} for about 30 min. Current was fed into the cell through two Pt electrodes. Measurements were carried out in 1.0, 10, 30, 70 and 100 mM NaCl solutions which were prepared from p.a. NaCl and deionized water (Millipore Milli-Q). The system was equilibrated with the appropriate electrolyte solution overnight.

In the donor chamber the reference electrode was placed in a Luggin capillary close to the surface of the array. In the acceptor chamber the reference electrode was connected to the cell via a salt bridge, consisting of 0.5 M NaCl with 3 wt.% of Agar gel. The salt bridge was used because the resistance between the current and reference electrodes became too large when the reference electrode was placed in a Luggin capillary, and also because it is preferable not to expose the reference electrode to an electric field.

Before each measurement the potential difference between the reference electrodes due to the concentration difference between the solution and the salt bridge was adjusted so that no current passed through the cell. The polarization curves were measured with a sweep rate of 1 mV s^{-1} to obtain a virtually stationary state. The sign of the potential was chosen so that the cations moved from the donor chamber through the microhole array and the cation exchange membrane into the acceptor chamber. The potential sweeps ended at the potentials -1200 to -1800 mV vs. open circuit. Solutions were not stirred during the measurements. Each measurement was made in fresh solution but the position of the microhole array and the membrane remained the same in each measurement because the cell was not opened. Due to low electric currents no special care had to be taken because of products of the electrolysis.

4. RESULTS AND DISCUSSION

A typical I–V curve corresponding to a NaCl concentration $c^b = 1.0$ mM is given in Fig. 3. The limiting current can be obtained as the current at the end

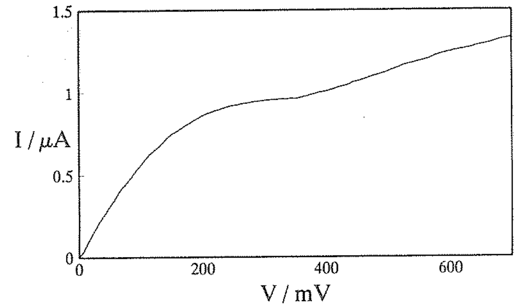

Fig. 3. A current–voltage curve for the NaCl concentration $c^b = 1.0\,\text{mM}$. The observed limiting current was $I_L = 0.96\,\mu\text{A}$.

of the plateau region, which gives $I_L = 0.96\,\mu\text{A}$ in this case. As anticipated, the use of the microhole array leads to a clear determination of the limiting current which is necessary to unambiguously find out the corresponding transport numbers at the different concentrations. A clear plateau region can also be obtained without a microhole array when employing a sufficiently small exposed area[19] but in that case the exact value for the thickness of the DBL is not known, as it is in the present method.

Table 1 gives the observed limiting currents at the bulk solution concentrations employed. These limiting currents were obtained from the corresponding plateaus of I–V curves similar to that in Fig. 3.

The transport numbers of the membrane system t_1^s can now be obtained from the measured values of I_L and equation (12). The porosity at the microhole array, ε, appearing in this equation can be estimated from the diameter of the pores and the parameter of the hexagonal lattice as $\varepsilon \approx 0.02$. However, a higher degree of accuracy is needed if transport numbers are to be obtained from the comparison between theory and experiment. Thus, we introduce the reasonable assumption that the transport number corresponding to $c^b = 1.0\,\text{mM}$ is exactly one and evaluate the quotient $\varepsilon A_g FD/[(1 - t_1^s)\delta]$ from this assumption. The last column in Table 1 shows the transport numbers t_1^s obtained at the other concentrations. As expected, these values decrease with the concentration c^b due to the increasing participation of co-ions in the migrational transport when the concentration is increased[20, 21].

The transport numbers measured in this way are usually called "apparent" transport numbers because they incorporate the effect of the solvent flow (mainly electro-osmotic in nature) through the membrane. Since we are measuring the transport numbers at a high current density (in particular, at the limiting current density) it could be expected that corrections for electroosmosis would be important[20, 22]. However, this is not our case because of the relatively low concentrations here employed (1.0–100 mM). Therefore, the transport numbers in Table 1 can be considered as the true transport numbers corresponding to the membrane system.

Table 1. Experimental limiting currents (I_L) and sodium transport numbers (t_1^s) at the bulk concentrations (c^b) employed

c^b(mM)	I_L(μA)	t_1^s
1.0	0.96	1*
10	11	0.924
30	36	0.880
70	100	0.803
100	160	0.760

* See text.

It is well known that the transport numbers of the membrane system are usually smaller than those of the membrane due to the effect of back diffusion[20, 23]. The difference between t_1^s and t_1^m can approximately be estimated by simple order of magnitude analysis. According to the Donnan exclusion theory[14], the co-ion concentration inside the membrane is $\bar{c}_2 \approx (c^b)^2/\bar{X}$ where $\bar{X}$ is the fixed charge concentration in the membrane, and bars denote quantities related to the membrane phase. The back diffusion flux can then be estimated as

$$\frac{\bar{D}_2(c^b)^2}{d\bar{X}} \sim (10^{-10}\text{–}10^{-9})\,\text{mol cm}^{-2}\,\text{s}^{-1} \qquad (13)$$

$d \approx 10^{-2}\,\text{cm}$ is the membrane thickness, $\bar{X} \approx 1\,\text{M}$ and $\bar{D}_2 \approx (10^{-7}\text{–}10^{-6})\,\text{cm}^2\,\text{s}^{-1}$[24, 25]. The value $c^b = 0.1\,\text{M}$ has been considered in equation (13) since this is the case when the back diffusion effects will be more important. The back diffusion flux must be compared now with the cation flux, which can be estimated as

$$J_1 \approx \frac{i_L}{F} \approx \frac{I_L}{A_g F} \approx 5 \times 10^{-8}\,\text{mol cm}^{-2}\,\text{s}^{-1} \qquad (14)$$

where $A_g \approx 0.031\,\text{cm}^2$, and $I_L = 160\,\mu\text{A}$ for $c^b = 0.1\,\text{M}$ (see Table 1). It is concluded from equations (13) and (14) that the correction for back diffusion (*ie* the difference between t_1^s and t_1^m) does not exceed the experimental error in the determination of the limiting current. Consequently, we can neglect the effect of back diffusion and take $t_1^s \approx t_1^m$.

Higher transport numbers than those obtained here are usually reported[21] for perfluorinated sulfonic acid membranes. However, it must be emphasized that the methods usually employed in these measurements make use of the so-called static or "zero-gradient" conditions, *ie* the concentration difference is $\Delta c = 0$ at time $t = 0$ in the Hittorf experiments, and $I = 0$ in the potentiometric determinations of the electromotive force. On the contrary, our values of the transport numbers have been obtained in the presence of large gradients. Other measurements performed under dynamic conditions (conductivity measurements) different from the ones here involved also yielded cation transport numbers smaller than usual ones but close to those shown in Table 1[3]. (See ref. [26] for a review on the existing methods used to measure transport numbers and their theoretical basis in terms of the Nernst–Planck equations.)

The transport numbers t_1^s in Table 1 are plotted against concentration c^b in Fig. 4. To obtain the theoretical values of t_1^s we can assume that the mem-

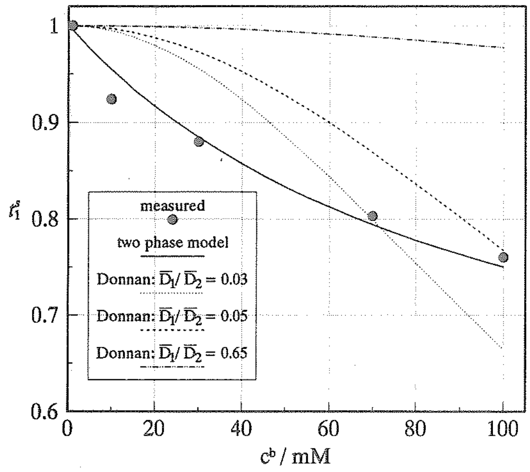

Fig. 4. Transport numbers vs. NaCl concentration in the bulk solutions. The points correspond to the experimental values and the curves to the theoretical values obtained from equation (16) (patterned lines) and equation (17) (solid line).

brane solution is homogeneous and write[14]

$$t_1^m = \frac{\bar{D}_1 \bar{c}_1}{\bar{D}_1 \bar{c}_1 + \bar{D}_2 \bar{c}_2}. \tag{15}$$

The ion concentrations inside the membrane, $\bar{c}_i$, can be obtained from the classical Donnan theory and equation (15) then reads

$$t_1^m = 1 - \left\{ 1 + \frac{\bar{D}_1}{\bar{D}_2} \left[\frac{\bar{X}}{2c^b} + \sqrt{\left(\frac{\bar{X}}{2c^b} \right)^2 + 1} \right]^2 \right\}^{-1}. \tag{16}$$

The convex curves in Fig. 4 have been obtained by introducing $\bar{X} = 0.8\,\mathrm{M}$ and $\bar{D}_1/\bar{D}_2 = 0.03$, 0.05 and 0.65 in equation (16). However, all the choices of parameters would give the same trend: the form of the theoretical curve t_1^s vs. c^b is always convex, and therefore, agreement between theory and experiment is not possible. This result is connected to the asymptotic behaviour $\bar{c}_2 \rightarrow (c^b)^2/\bar{X}$ for $c^b/\bar{X} \ll 1$[25].

Given the structural heterogeneity of the Nafion membrane, the failure of the homogeneous Donnan theory to describe the experimental results is not surprising[27]. Several theoretical modesl have been proposed to describe the effects of the Nafion cluster network structure on the membrane transport properties. In particular, absolute rate theory and percolative approaches have been employed[27]. Alternatively, the pore model has also been invoked since Koh and Silverman[28] showed that the low co-ion transport rate could be explained by restricted transport in narrow membrane pores (see also [29] and references therein). Capeci *et al.*[30] incorporated the available structural information of the Nafion membranes into a pore approach when modelling ion transport in concentrated solutions (1–5 M). In this concentration range, there are two clearly differentiated regions. In the vicinity of the cluster walls, the co-ion is virtually excluded while in the central region of the cluster the solution concentration is that of the external electrolyte. It is interesting to note, however, that the usual pore network models (which consider the membrane as a bundle of identical pores) would not describe our results, because the co-ion is almost completely excluded from the pore in the dilute concentration range here considered (1.0–100 mM).

An alternative approach is to model the structural heterogeneity considering that the pores are not all identical. Instead, there will be a distribution of pore sizes and surface charge densities in the membrane. A simpler way of modelling this effect is to assume that a fraction f or pores contain a high concentration of charged groups while the remaining fraction $(1-f)$ are uncharged pores. Similar models have recently been used by Petropoulos for cellulose membranes[31], by Cwirko and Carbonell[29] for Nafion membranes, and Tugas *et al.*[32], and could be regarded within a general approach which considers a heterogeneous membrane as a system of two or more conducting phases, the transport properties of the membrane being a function of the corresponding phase properties[25]. Taking into account the above ideas, we can regard the Nafion membrane as consisting of two conductive phases, and generalize equation (16) to

$$\begin{aligned} t_1^s &= \frac{f\bar{D}_1 X + (1-f)D_1 c^b}{f\bar{D}_1 X + (1-f)(D_1 c^b + D_2 c^b)} \\ &\simeq 1 - \left[2 + \frac{f\bar{D}_1 X}{(1-f)D} \frac{1}{c^b} \right]^{-1}. \end{aligned} \tag{17}$$

In the first phase (with volume fraction f), the fixed charge concentration X, which is related to the average membrane value $\bar{X}$ through $X = \bar{X}/f$, is high enough to completely exclude co-ions so that $c_1 \approx \bar{X}$ and $c_2 \approx 0$. In the second phase (with volume fraction $1-f$), ion concentrations and diffusion coefficients are the same as in the bulk solution, $c_1 = c_2 = c^b$ and $D_1 \approx D_2 \equiv D$.

Under these assumptions, equation (17) has only one free parameter, the factor multiplying $1/c^b$, and can now be fitted to the experimental points. This has been done in Fig. 4 (solid curve). This approach gives a good account of the experimental observations when $f\bar{D}_1 X/(1-f)D = 0.2$. This could correspond, *eg* to the values $f \approx 0.8$, $X = 0.8\,\mathrm{M}$ ($X = 1\,\mathrm{M}$) and $\bar{D}_1/D \approx 0.05$, which are similar to those usually found in the literature[29, 33–35]. More important than this agreement is the fact that equation (17) properly accounts for the observed concave shape of the t_1^s vs. c^b plot.

5. CONCLUSIONS

We have presented an improved method of measuring limiting currents in cation exchange membranes, and applied it to the Nafion 117 membrane in dilute aqueous NaCl solutions. The method is based on the use of a microhole array attached to the surface of the membrane, and leads to a clear determination of the limiting current I_L along with the exactly defined thickness of the depleted diffusion layer. From the values measured for I_L we have obtained information on the cation transport number t_1^s when the membrane operates at the limiting current conditions. These special conditions are judged to be responsible for the relatively small values found for t_1^s when compared to those obtained by other methods. The classical Donnan theory for homogeneous membranes was found to be unable to explain the observed values for t_1^s. Instead, a simple two phase model accounting for the different conductive phases in the membrane was able to describe the experimental trends over the concentration range studied.

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