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Synthesis, Characterization and Conductance Studies of Inorganic Precipitate Synthetic Membrane

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ABSTRACT

The electrical conductivity of simple metal ions across the parchment supported lead tungstate membrane bathed in different concentration of 1:1 electrolytes (KCl, NaCl and LiCl) at several temperature ranges are reported. Absolute reaction rate theory has been applied to derive various thermodynamic parameters, Ea, $\Delta H^{\neq}, \Delta F^{\neq}$ *and* $\Delta S^{\neq}$*. The activation energies are found to depend on the size of penetrant species and decrease with the increase in the concentration of the bathing solutions. It is concluded that the membrane is weakly charged and ionic species retain their hydration shell at least partially, while diffusing through the membrane pores. The values of* $\Delta S^{\neq}$ *are negative indicating, that partial immobilization of ions takes place probably due to the interstitial permeation and ionic interaction with the fixed charge groups of the membrane skeleton. The membrane has been characterized on the basis of thickness, porosity, water uptake and swelling. The membrane has also been characterized on the basis of scanning electron microscopy (SEM) and Fourier transformed infrared (FTIR) analysis.*

Keywords: Conductance, thermodynamic parameters, lead tungstate membrane.

INTRODUCTION

In recent years membrane technology has obtain much attention in the industry and also in daily life. [1,2]. Among the various kinds of membranes, ion exchange membranes have been widely studied and applied as active separators in divers ractically driven processes, such as electrolysis for desalting of brackish water, reconcentrating brine from sea water and production of table salt. The inorganic ion exchange materials besides other advantages are important being more stable to high temperature and radiation field than the organic ones [3]. The basic applications of the ion exchange membrane process are based on the Donnan membrane equilibrium principle and have been paid attention to solve two important environmental problems, for the recovery and enrichment of valuable ions, and the removal of undesirable ions from waste water [4]. In this paper we describe the application of absolute reaction rate theory to the membrane conductance data at different temperatures for investigating the mechanism of ion transport. Various thermodynamic parameters namely energy of activation E_a, free energy of activation $\Delta F^{\neq}$, enthalpy of activation $\Delta H^{\neq}$, entropy of activation $\Delta S^{\neq}$ of the membrane electrolyte system have been determined at different temperatures in order to understand the mechanism of ion transport through the membrane.

MATERIALS AND METHODS

Membrane preparation: Parchment supported inorganic precipitate lead tungstate model membrane has been prepared by the method of interaction as suggested by Ansari and coworkers [5,6]. To precipitate these substances in the interstices of parchment paper, a 0.2M solution of sodium tungstate (S. d. Fine Ltd.) was placed inside glass tube, to one end of which was tied the parchment paper (supplied by Amol group of Companies, Mumbai, India) previously soaked in deionised water. The tube was suspended for 72 hours in a 0.2 M solution of lead nitrate (Ranbaxy). The two solutions (fresh solution) were interchanged later and kept for another 72 hours. Thus parchments paper and inorganic precipitate as a whole acts as a model membrane. The membrane thus prepared was washed with deionized water to remove free electrolytes.

Measurement of membrane conductance: The membrane was sealed between two half cells The half cells were first filled with electrolyte solutions (KCl, NaCl or LiCl) to equilibrate the membrane (Fig. 1). The solutions were replaced by purified mercury without removing the adhering surface liquids. The trapped air, if any, was removed from the membrane-solution interface in order to get reproducible results. Platinum electrodes were used to establish electrical contacts. The membrane conductance were monitored on a direct reading conductivity meter 303 (Systronics) at a frequency of 10^3 Hz. All measurements were carried at 20^0, 25^0, 30^0 and 35^0 ($\pm 0.1^0$C) . The electrolyte solutions were prepared from AR reagents in deionized water.

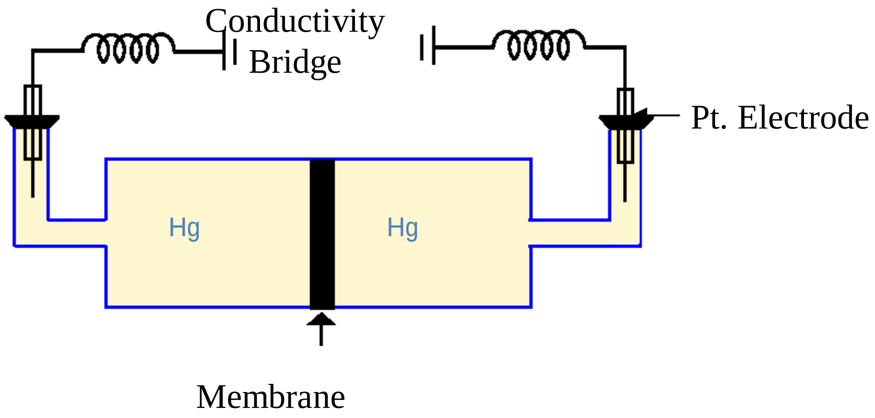

Fig. 1 Cell for measuring electrical conductivity of membrane

Characterization of Membrane: The expected performance of an ion exchange membrane is its complete characterization, which involves the determination of all those parameters that affect its electrochemical properties. These parameters are the membrane water content, porosity, thickness, swelling etc. and were determined as described elsewhere [7].

Water uptake (% total wet weight): The membrane was soaked in deionized water for 2 hour. blotted quickly with Whatman filter paper to remove surface moisture and immediately weighted. These were further dried to a constant weight in vacuum over P_2O_5 for 24 hour. The water uptake (total wet weight) was calculated as follows

$$\%\ \text{total wet weight} = \left(\frac{W_w - W_d}{W_w}\right) \text{x}100 \qquad (1)$$

Where W_w is the weight of the soaked or wet membrane and W_d the weight of the dry membrane.

Porosity: Porosity was determined as the volume of water incorporated in the cavities per unit membrane volume from the water uptake data:

$$\text{Porosity} = \left(\frac{W_w - W_d}{AL\,\rho_w} \right) \qquad (2)$$

Where A is the area of the membrane (cm^2). L the thickness of the membrane (cm) and ρ_w the density of water (g/cm^3).

Thickness: The membrane thickness value was averaged from six measurements different locations on the effective surface region of the membrane using a micrometer.

Swelling: Swelling was measured as the difference between the average thickness of the membrane equilibrated in 1M NaCl for 24 hour and the dry membrane.

Scanning Electron Microscopy (SEM): The surface morphology of lead tungstate membrane was analysed with scanning electron microscope (SEM) model Philips 515 USA. Gold Sputter coatings was carried out on the desired membrane sample at pressure 1 Pa.

Fourier Transformed Infra Red (FTIR) Studies: The FTIR spectrum of parchment supported lead tungstate membrane was done by Perkin Elmer instrument model spectrum BX series USA The entrance and exit beam to the sample compartment was sealed with a coated KBr window and these was a hinged cover to seal it from the environment.

RESULTS AND DISCUSSION

The results of water content, Porosity thickness and swelling of parchment supported inorganic precipitate lead tungstate membrane are summarized in Table 1. The water content of a membrane depends on the vapor pressure of the surroundings. In case of most of the transport measurements, Only the membrane water content at saturation is needed, and that too mostly as a function of solute concentration. Thus low order of water content swelling and porosity with less thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites [8,9].

Table 1. Thickness, water content, Porosity and swelling properties of lead tungstate synthetic membrane

Thickness of the membrane (cm)	0.085
Water content as % weight of wet membrane	0.071
Porosity	0.114
Swelling of % weight wet membrane	0.09

The SEM surface image of parchment supported lead tungstate membrane is presented in fig. 2. It can be seen that the membrane is heterogeneous in nature as well as dense with no visible cracks. SEM images (fig. 2) appears to be composed of dense and loose aggregation of small particles and formed pores probably with non-linear channel but not fully inter connected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes.

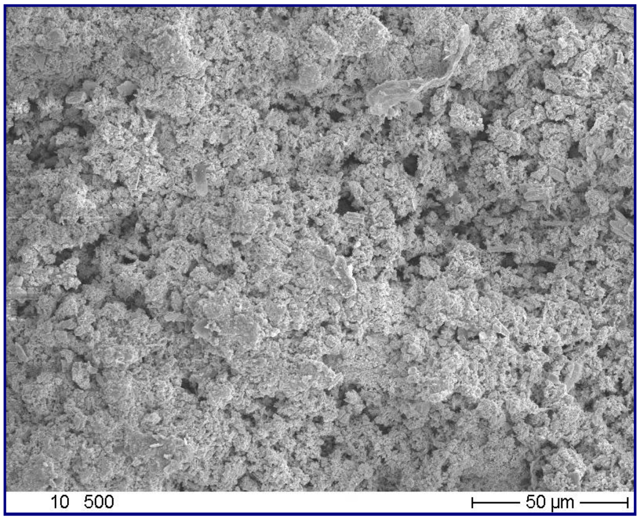

Fig. 2 Scanning electron micrographs (SEM) of parchment supported lead tungstate membrane

The FTIR spectra of the parchment supported membrane has provided in fig. 3. The membrane contains various characteristic peaks. The spectra exhibits various strong to medium or weak intensity band, such as 3421, 2919, 2851, 2425, 1765, 1383 and 1621 (Cm^{-1}) characteristic of the functions present in the inorganic precipitate membrane.

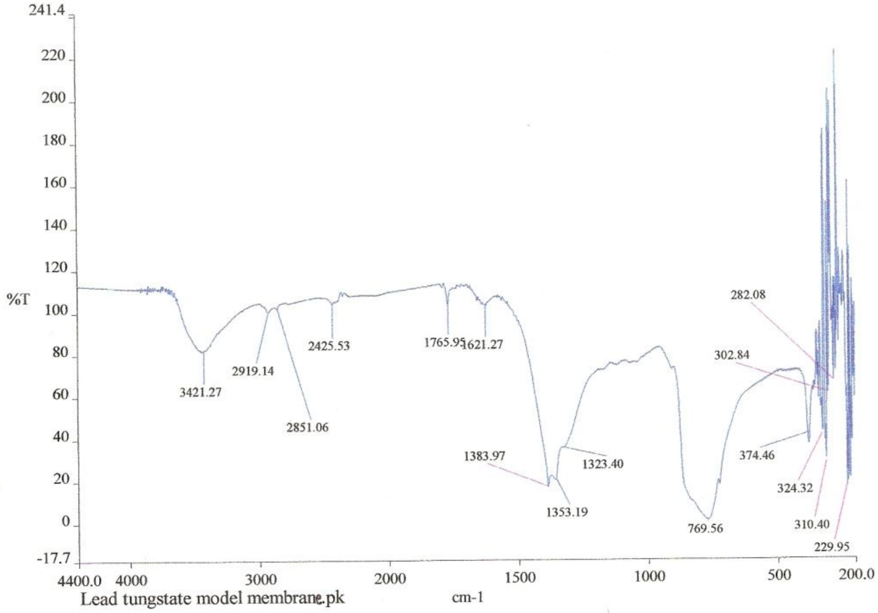

Fig. 3 FTIR Spectra of parchment supported lead tungstate membrane

The conductance of lead tungstate membrane bathed in lithium and sodium chloride solutions of different concentrations measured at different temperatures are given in table 2 whereas typical data for potassium chloride are depicted in fig. 4. These data show that the specific conductance of the membrane increases with increase in the concentration of the electrolyte and attains a maximum limiting value.

Table 2. The experimentally observed values of specific conductance $\left(m\Omega^{-1}cm^{-1}\right)$ for 1:1 electrolytes at various concentrations and temperatures across parchment supported lead tungstate membrane.

Electrolyte	**Concentration (Mol. dm^{-3})**	**Temperature (±0.1^{0}C)**			
		20	**25**	**30**	**35**
KCl	0.1	8.4	9.3	9.5	9.7
	0.01	8.1	7.4	7.6	9.1
	0.001	3.2	5.2	6.8	8.3
	0.0001	2.8	3.5	4.3	5.4
NaCl	0.1	6.9	6.8	6.8	8.8
	0.01	4.1	5.9	6.9	7.6
	0.001	2.9	4.3	5.2	5.8
	0.0001	2.1	2.3	3.1	3.7
LiCl	0.1	6.2	5.8	6.9	7.2
	0.01	3.2	5.6	6.1	6.7
	0.001	1.9	3.3	4.6	4.9
	0.0001	1.5	2.5	2.8	3.2

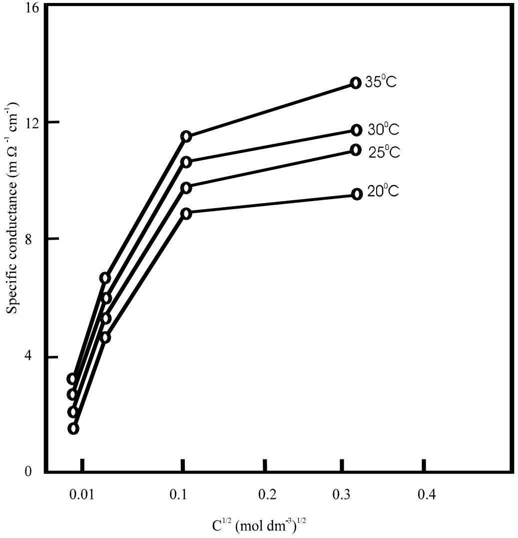

Fig. 4. Plots of specific conductance $(m\Omega^{-1}\,cm^{-1})$ against square root of concentrations (mol dm^{-3})$^{1/2}$ for KCl at different temperature through lead tungstate membrane

This is in accordance with the findings of lijima et al. [10] for nylon membrane with various alkali chlorides. The sequence of membrane conductance for the alkali metal ions under the same condition is $K^+ > Na^+ > Li^+$, similar to their ionic radii order. Similar behaviour was observed by several investigators for certain synthetic membranes[11-15]. This sequence indicates that the size of the ions is the major factor in the diffusion process. Membrane porosity in relation to the size of the species (Hydrated) flowing through the membrane seems to determine the above sequence. Although the sizes of the hydrated electrolytes are not known with certainty, there are few tabulations [16,17] of the number of mol of water associated with some electrolyte. However, in Fig. 5 a plot of specific conductance of different electrolytes (Chlorides) against free energy of hydration of cation [18] is given for the membrane.

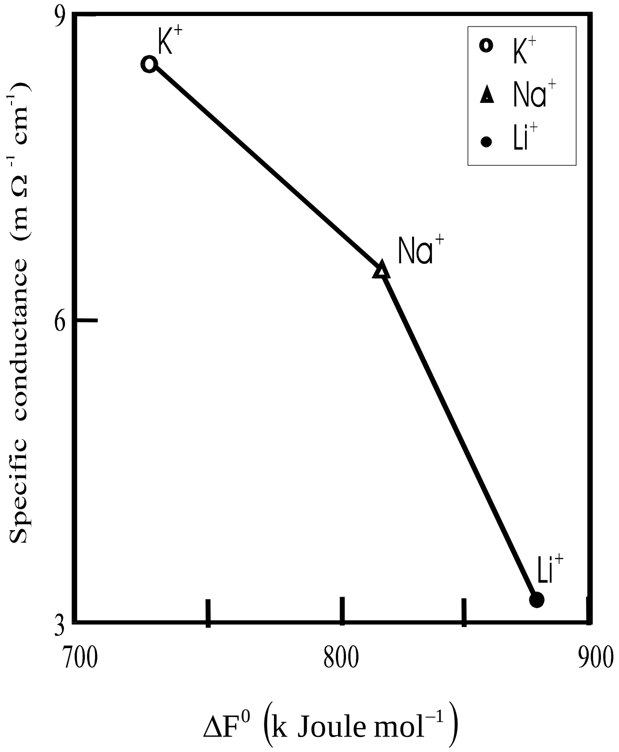

Fig. 5

Specific conductance ($m\Omega^{-1}cm^{-1}$) of various 1:1 electrolytes at 25^0C through lead tungstate membrane plotted against the free energy of hydration, ΔF^0 (k Joule mol^{-1}) of cations

It is seen that specific conductance decreases with increasing hydration energy, i.e. greater size due to increase in hydration. This points to the fact that the electrolyte is diffusing along pores or channels of dimensions adequate to allow the substance to penetrate the membrane. The state of hydration of the penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction of the total number of given kind would possess excess energy ($\Delta E^{\neq}$) per mol according to the Boltzmann distribution $f = e^{-\Delta E^{\neq}/RT}$ (R is the gas constant). Under these circumstances, those ionic species which have lost sufficient water of hydration and thus are smaller in size than the size of the pore would enter the membrane. This way the specific conductance would increase with increase in temperature, provided the membrane has undergone no irreversible change in its structure. That no such structural change involved is evident form the linear plots of log versus 1/T show in Fig. 6 the slope of which give the energy of activation as required by Arrehenius equation. A reference to Table 3 shows that the activation energy decreases with increase in concentration of the bathing electrolyte solution and that for different electrolytes at a particular concentration it follows the order : $E_aK^+ > E_aNa^+$

$> E_a\text{Li}^+$, analogous to the sequence of crystallographic radii of the alkali metal cations. When the penetrant moves in a polymer substance containing relatively small amount of water, its motion may be governed by the segmental mobility of the polymer and its diffusivity may depend on the probability that the segment will make a hole large enough to accommodate a penetrant species [19]. In such a system the activation energy will depend on the size of the penetrant species, i.e. the activation energy will increase with the penetrant size. If this is the case in our system, the dependence of the activation energy on the kind of alkali metal ion may be interpreted in terms of the ion's crystallographic radius, which is consistent with the result obtained in the diffusivity measurement in the same system [20].

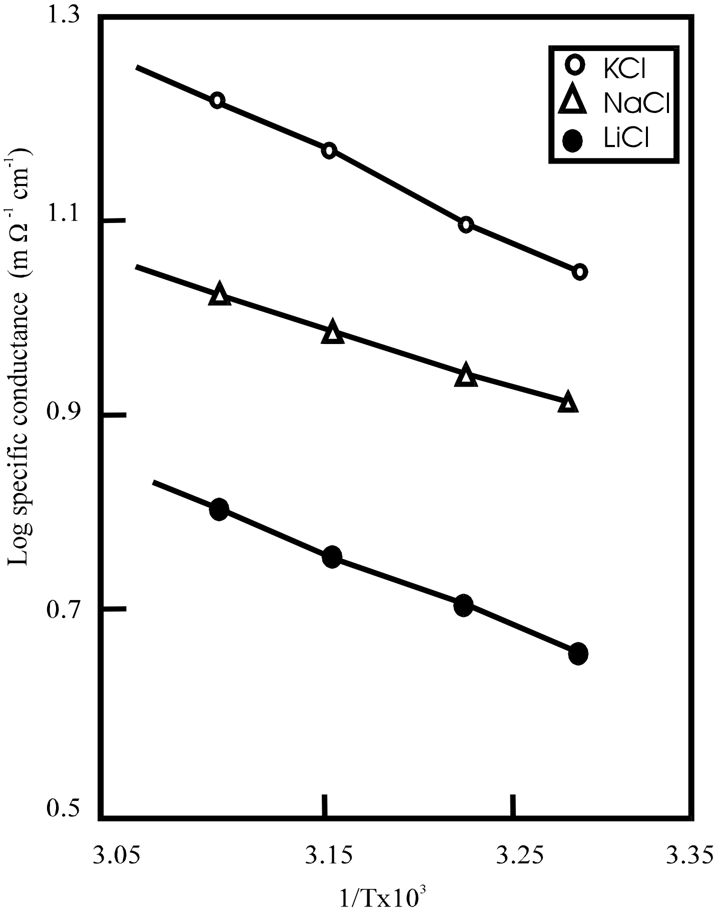

Fig. 6
Arrhenius plots of specific conductance

Table 3. Thermodynamic parameters values for parchment supported lead tungstate membrane in contact with different concentrations of values 1:1 electrolyte solutions.

Electrolyte	**Concentration (Mol. dm^{-3})**	**Parameters**			
		Ea K cal mol^{-1}	$\Delta H^{\neq}$ **K cal mol^{-1}**	$\Delta F^{\neq}$ **K cal mol^{-1}**	$\Delta S^{\neq}$ **K cal mol^{-1}**
KCl	0.1	3.03	2.25	17.9	-52.30
	0.01	4.98	3.02	18.6	-53.34
	0.001	8.56	3.23	19.1	-54.16
	0.1	2.08	2.82	17.75	-54.29

NaCl	0.01	3.65	2.08	18.20	-54.24
	0.001	5.78	2.19	18.59	-54.18
LiCl	0.1	1.23	0.69	17.11	-52.88
	0.01	1.45	1.07	17.80	-54.75
	0.001	1.65	2.09	18.07	-54.93

The thermodynamic parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta F^{\neq}$ have been determined using the theory of absolute reaction rates. Following Eyring [21,22].

$$\pi = \frac{RT}{Nh} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/R} \qquad (3)$$

Where π is the membrane conductance, h the Planck constant, R the gas constant, N the Avagadro number and T the absolute temperature. $\Delta F^{\neq}$ is the free energy of activation for the diffusion of ions and is related by Gibbs- Helmoltz equation (4)

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (4)$$

$\Delta H^{\neq}$ is related to Arrhenius energy of activation, E_a by the relation (5)

$$E_a = \Delta H^{\neq} + RT \qquad (5)$$

A plot of log $\pi Nh/RT$ versus 1/T from experimental data is linear, the slope and the intercept of which give the value of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. This justifies the applicability of Eq. (3) to the system under investigation. The derived value of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were then used to get the value of $\Delta F^{\neq}$and E_a using eqs (4) and (5). The values of E_a , $\Delta H^{\neq}, \Delta F^{\neq}$ and $\Delta S^{\neq}$ for the diffusion of various electrolytes through the membrane are given in Table 3. The results indicate that the electrolyte permeation gives rise to negative values of $\Delta S^{\neq}$. These values may be attributed to the partial immobilization of ions within the membrane most notably due to interstitial permeation and ionic interaction with the membrane fixed charge group.

The values of $\Delta S^{\neq}$ are significantly decreased by an increase of concentration and temperature [23] and that is attributed to the disturbance of the solvent structure and an improved arrangement of the molecules in the ion hydration shell. According to Eyring [21], the values of $\Delta S^{\neq}$ indicate the mechanism of flow and large positive $\Delta S^{\neq}$ is interpreted to reflect the breakage of bonds, while low and negative values of entropy of activation indicate that would be possible only if the activation state involves formation of some bonds between the diffusing ion and the membrane material. High $\Delta S^{\neq}$ value associated with the high value of E_a for diffusion may suggest the existence of either a large zone of activation or loosening of more chain segments of the membrane. On the other hand low values of $\Delta S^{\neq}$ imply either a small zone of activation or no loosening of the membrane structure upon permeation [24].

APPLICATIONS

The synthesis of inorganic composites has received a great deal of attention because it provided new materials with special mechanical, chemical and electrochemical properties. Parchment paper is one of the most attractive material use in the field of chemistry, biological and medical sciences, food industry etc. due to its excellent chemical and physical properties such as transparent, nontoxic, low adsorptive towards small drug molecules.

The theory of absolute reaction rate can be applied to the diffusion processes in membranes, Absolute reaction rate theory provides a model of the transfer process envisioning diffusion as the (Jumping) of solute molecules with associated activation energy between the vacancies with in the solvent lattice. This theory has further been extended to predict that the ratio of diffusivity in a dilute solution to its rate in pure bulk liquid.

CONCLUSIONS

The parchment supported lead tungstate membrane was prepared and found to be quite stable. The membrane were analysed for alteration in colour, texture, decomposition, crakes, and holes. The surface morphological structure of the membrane was also observed with the aid of scanning electron microscope. Particles are irregularly condensed and adopt the heterogeneous structure composed of masses of various size. The electrical conductance of ions across parchment supported lead tungstate membrane were measured with univalent electrolyte solutions with platinum electrode. The conductance measurements of various electrolytes were found to follow the sequence for the cations $K^+ > Na^+ > Li^+$. The sequence for energy of activation is $E_aK^+ > E_aNa^+ > E_aLi^+$. The activation energies are found to decrease with the increase in the concentration of the bathing solutions. It is concluded that the membrane is weakly charged.

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