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Synthesis, estimation of stability in different media, electrochemical properties and potentiometric studies of PVC-based NP ion-exchange composite membrane for desalination and waste water treatment applications

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ABSTRACT

The chemical stability of PVC-based Neodymium phosphate (NP) ion-exchange membrane shows better results with strong oxidizing agent $KMnO_4$ as compared to the acidic and alkaline medium and it was synthesized by sol–gel and die casting method. The characterization of the ion-exchange composite membrane was carried out by employing Fourier transform infrared spectroscopy, thermogravimetry analysis and scanning electron microscopy. The membrane with 25% PVC and 75% NP shows excellent mechanical and thermal stability as well as good ion-exchange capacity. The observed membrane potential data were used to determine the transport number of cation and anion and other electrochemical parameters of the composite membrane. The prepared membrane can be considered as an excellent material for desalination and wastewater treatment applications.

Keywords: Ion-exchange membrane; Chemical stabilities; Electrochemical properties; Transport number; Charge density; Desalination applications

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1. Introduction

At present, ion-exchange membrane is most widely used in desalination technology and shows great attention to both academic and industrial areas due to their multi-purpose applications including wastewater treatment, metal ion recovery, electrolysis process and treating industrial and biological effluents. It also plays an important role in food and pharmaceutical processing [1–5].

The application of inorganic ion-exchange material is not only due to their good chemical, mechanical, thermal stability and specific selectivity for ions but also useful for separation and material science. However, the organic ion-exchange materials have a broad applicability, but there are a few limitations of these membranes because of their poor thermal and mechanical stability and the removal capability of ordinary organic ion-exchange resins is likely to decrease under high temperature condition. These membranes are rather insignificant due to their high cost and other demerits, such as relatively poor electrochemical properties, large pores and low selectivity for particular ions than the ion-exchange composite membranes [6–10].

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For desalination and wastewater treatment applications, polymer-based ion-exchange membranes are still limited because they have some general drawbacks, including insufficient mechanical, chemical, thermal stabilities and high cost [11–15].

In this study, we focus on the preparation of ion-exchange composite membrane, a commercial organic polymer; PVC was selected as the polymer matrix of the ion-exchange membrane due to its excellent performances like better chemical, thermal and mechanical properties at low cost.

Thereafter, the novel composite membrane was prepared by introducing Neodymium phosphate (NP) into PVC polymer thus becoming a strategic tool for further study of new ion-exchange composite material. The hybrid membrane is expected to possess better strength of the inorganic materials and enhanced stability in acidic, alkaline and strong oxidant media with minimized effects on other properties such as ion-exchange capacity and functionalities of the PVC composite membrane.

2. Experimental

2.1. Materials

Neodymium chloride, trisodium phosphate, calcium (II) chloride, magnesium (II) chloride, barium (II) chloride, HCl, NaCl, HNO_3, H_2SO_4, NaOH, $KMnO_4$ and PVC were obtained from E. Merck, Mumbai, India. All other reagents used were of analytical reagent grade.

2.2. Synthesis of composite membrane

NP precipitate was prepared by the mixing of 100 ml solution of each 0.2 M neodymium chloride and 0.2 M trisodium phosphate. The precipitate was washed well with deionized water to remove free reactants and then dried and powdered. The membrane was prepared by using (1:3) wt/wt ratio of binder (PVC) and NP. The precipitate was ground into a fine powder and was sieved through 200 mesh (granule size < 0.07 mm). The PVC was also ground and sieved through 200 mesh. The mixtures were then kept in a pellet casting die having a diameter of 2.45 cm and placed in an oven maintained at 200°C for about an hour to equilibrate the reaction mixture [3,5]. The die containing the mixture was then transferred to a pressure device, and 100 MPa of pressure was applied during the fabrication of the membrane. The membrane was subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface and only those which had a smooth surface and generate reproducible potentials were considered. The PVC was selected because of its polymeric structure, durability and flexibility that provide adequate adhesion to the NP which accounts for the mechanical stability and performance of the composite membrane. Therefore, it is efficient, cost-effective and flexible which shows good selectivity.

2.3. Characterization of PVC-based NP composite membrane

2.3.1. Method for measurements of chemical stability, thickness and ion-exchange capacity of composite membrane

The ion-exchange capacity was determined by the titration method. One gram of the dry cation exchanger in the H^+ form was taken into a glass column having an internal diameter (1 cm) and fixed with glass wool support at the bottom. The bed length was approximately 1.5 cm long. One-molar $NaNO_3$ as eluent was used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 mL min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the ion-exchange capacity was determined. To estimate its chemical stability the membrane was exposed to acidic (1 M H_2SO_4), basic (1 M NaOH) and strong oxidant media (1 M $KMnO_4$) solutions. The thickness of the membrane was measured by taking the average thickness of the membrane using screw gauze [16,17].

2.3.2. SEM studies of the composite membrane

The surface morphology of the composite membrane was observed on a ZEISS EVO Series Scanning Electron Microscope EVO 50 at an accelerating voltage of 20 kV. The sample was mounted on a copper stub and sputter coated with gold to minimize the charging effect. The scanning electron microscopic image was taken to confirm the microstructure of the composite membrane.

2.3.3. TEM analysis of the composite membrane

The transmission electron microscopy (TEM) image of the composite membrane was obtained by a transmission electron microscope at 4,000 k magnification. TEM analysis was carried out to indicate the particle size of PVC-based NP composite membrane.

2.3.4. FTIR studies

The Fourier transformed infrared (FTIR) spectrum of PVC-based NP composite membrane was done by interspec 2020 FTIR spectrometer, spectrolab (UK). The sample compartment was 200 mm wide, 290 mm deep and 255 mm high. The entrance and exit beams to the sample compartment were sealed with a coated KBr window and there was a hinged cover to seal it from the environment.

2.4. Electrochemical studies of the composite membrane

2.4.1. Measurement of membrane potential

The PVC-based NP composite membrane was placed at the centre of the glass tube cell for measuring membrane potential. The half cell contains 25 ml of electrolyte solution even though the capacity of each of the half cells holding the membrane was about 35 ml. The various salt solutions (chlorides of Ba^{2+}, Ca^{2+} and Mg^{2+}) were prepared using deionized water. Both the collared glass containers had a cavity for introducing the electrolyte solution and saturated calomel electrodes. The electrolyte solutions in both the tubes were stirred by magnetic stirrers at constant 500 rpm to minimize the effect of boundary layers on membrane potential. Thereafter, the membrane potential difference across the composite membrane was measured with the help of digital potentiometer (EI India). The electrochemical setup for membrane potential measurements may be depicted as (Fig. 1).

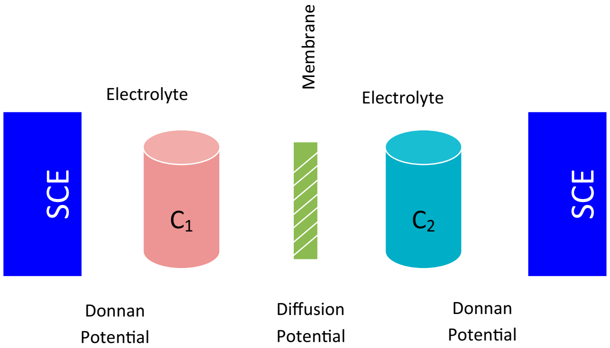

Fig. 1. The electrochemical setup for membrane potential measurements.

2.4.2. Determination of the electrochemical parameters

The electrochemical parameters such as transport numbers, mobility ratio and surface charge density of the PVC-based NP composite membrane electrolyte system have been determined using Nernst equation and TMS method in order to understand the mechanism of ion transport through the membrane [18–21].

$$\Delta\bar{\psi}_m = \frac{RT}{F}(t_+ - t_-)\ \ln\frac{C_2}{C_1} \tag{1}$$

$$\Delta\bar{\Psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\bar{D}^2}+\bar{D}}{\sqrt{4C_2^2+\bar{D}^2}+\bar{D}} + \bar{U}\log\frac{\sqrt{4C_2^2+\bar{D}^2}+\bar{D}\bar{U}}{\sqrt{4C_1^2+\bar{D}^2}+\bar{D}\bar{U}}\right) \tag{2}$$

$$\bar{U} = (\bar{u}-\bar{v})/(\bar{u}+\bar{v})$$

where $\bar{u}$ and $\bar{v}$ are the ionic mobilities of cation and anion ($m^2\ v^{-1}\ s^{-1}$), respectively, in the membrane phase, C_1 and C_2 are the concentrations of the membrane and $\bar{D}$is the charge on the membrane expressed in equivalent per litre.

3. Results and discussion

The ion-exchange capacity gives information about the charge density in the composite membrane, which is a key parameter, connected to the transport phenomena of the membrane. The thickness and ion-exchange capacity of PVC-based NP composite membrane were found to be 0.092 mm and 1.4 meq g^{-1}, respectively. The lowering of ion-exchange capacity with thickness of membrane implied that interstitial spaces are negligible and diffusion across the membrane would occur mainly through the exchange sites [22].

In order to examine the chemical stability of the PVC-based NP composite membrane, it was kept in different acidic, basic and oxidizing media. The membrane was found to be stable in acidic (1 M HNO_3), basic (1 M NaOH) and strong oxidizing ($KMnO_4$) media over a period of 25, 50 and 150 h. The membrane is most effective in strong oxidant ($KMnO_4$) media as shown in Table 1. However, the membrane shows some sign of rupture for a period longer than 150 h. Thus, the membrane can be used for food and pharmacy processing and for desalination applications [23].

A smart scanning electron microscopy (SEM) surface image of PVC-based NP composite membrane is shown in Fig. 2 and it is clear that the performance of the membrane strongly depends on surface morphology. The distribution of materials that is PVC and NP was uniformly mixed with each other and therefore, the prepared membrane has a homogeneous nature, which shows excellent results and applied for further studies. Moreover, the thermal treatment increases the NP particles' compatibility with binder PVC. It is revealed from the SEM micrograph that the surface of PVC-based NP composite membrane is just like flakes. The flakes would provide the three-dimensional surface area for the metal ions absorption. Thus, the transport of metal ions through this cation-exchange membrane would be impressive. Hence, the flake-like morphology can be very well utilized for the fabrication of wastewater treatment equipment.

A TEM image of the PVC-based NP composite membrane is shown in Fig. 3. It can be seen that the NP particles are consistently distributed on the surface of PVC. The average particle size is close to 18–20 nm, which is slightly higher than that determined by SEM. However, we could conclude from the TEM and SEM results that all the particles were relatively uniform and highly porous in nature [24,25]. The TEM image shows that the particle size in nano range would provide enhanced surface-to-volume ratio and hence a very small amount of the material would be sufficient to prepare the useful membrane for wastewater treatment that would decrease the economy of the wastewater treatment equipment.

The FTIR spectrum was used to study the structural characterization and bonds of the composite material. Fig. 4 shows the FTIR spectrum of PVC-based NP composite membrane. The spectrum shows two strong absorption peaks at 680 and 1,015 cm^{-1} due to the H–O–H bending of the water molecules. The sharp

Table 1
Observation of chemical stability of PVC-based NP composite membrane

PVC-based NP composite membrane along with different media	Observation time (hours) for preservation	Remarks	Efficiency (%) for desalination applications
PVC-based NP composite membrane with base (1 M NaOH)	25, 50 and 175	Stable	60
PVC-based NP composite membrane with acid (1 M H_2SO_4)	25, 50 and 175	Stable	80
PVC-based NP composite membrane with strong oxidant ($KMnO_4$)	25, 50 and 175	Fragile in 50 h and broken after 175 h	90

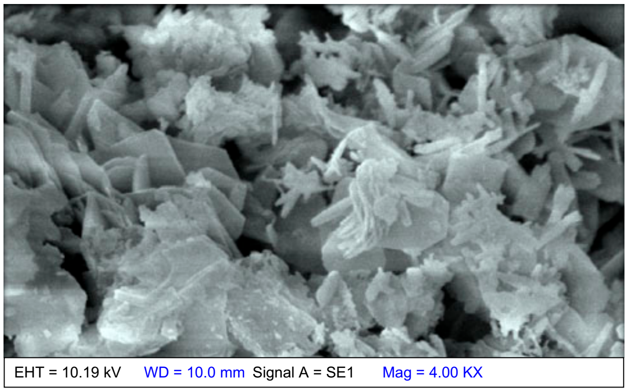

Fig. 2. Surface SEM image of PVC-based NP ion-exchange composite membrane (at magnification of 4.00K×).

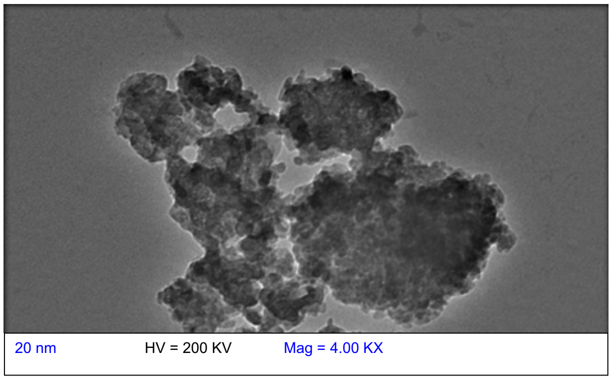

Fig. 3. TEM image of PVC-based NP ion-exchange composite membrane (at magnification of 4.00K×).

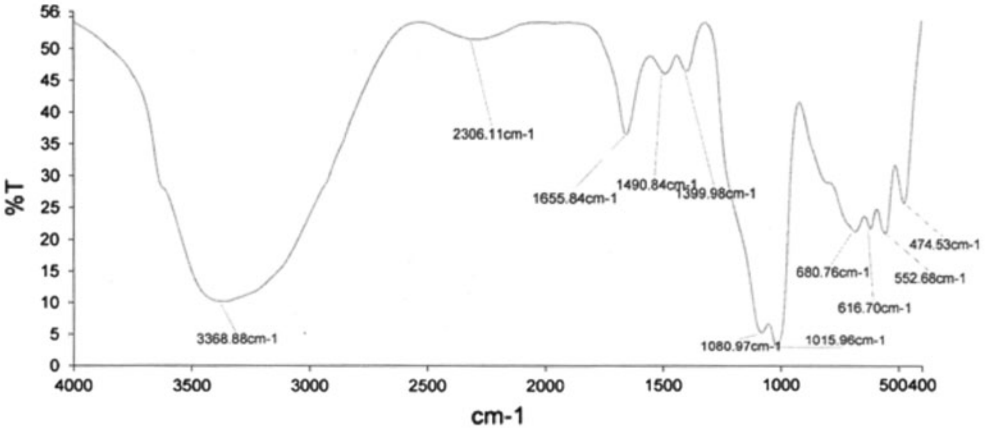

Fig. 4. FTIR Spectra of PVC-based NP ion-exchange composite membrane.

peak observed at around 1,490 cm^{-1} is attributed to the presence of a phosphate group and two sharp peaks 552 and 474 cm^{-1} may be due to presence of C–Cl bond and metal. The broadband in the region at 3,368 cm^{-1} may be due to the presence of external water molecules, which comes from the atmospheric moisture. The absorption peak at 2,306 and 1,655 cm^{-1} shows the C–H and C=C stretching, respectively [26].

The observed membrane potential data (standard error ± 0.01) obtained with PVC-based NP composite membrane using various divalent electrolytes is plotted as a function of –log C_2 (Fig. 5). The membrane potential depends on the electrolyte concentration, which increases with the decrease in external electrolyte concentration. This shows that the membrane was negatively charged and found to be cation selective. The membrane potential offered by various alkaline earth metal divalent electrolytes follow the order $MgCl_2 > CaCl_2 > BaCl_2$.

The transport number can be determined by means of potential differences, which develop across the composite membrane when the membrane separates two different electrolyte concentrations. The transport study of the membrane in various electrolyte solutions is an important parameter to further study the membrane phenomena. The Eq. (1) was used to get the values of transport number from the observed membrane potential data and subsequently, the mobility ratio $\bar{\omega} = \bar{u}/\bar{v}$ was calculated.

The transport number of cation (standard error ± 0.01) of the various electrolytes decreases with the increase in the concentration of various electrolytes and follow the decreasing order $MgCl_2 > CaCl_2 > BaCl_2$ as shown in Fig. 6.

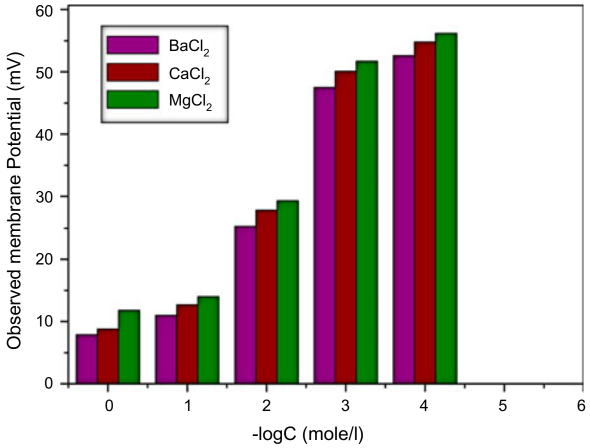

Fig. 5. Plots of observed membrane potentials against logarithm of concentration for PVC-based NP ion-exchange composite membrane using various electrolytes at 25˚C.

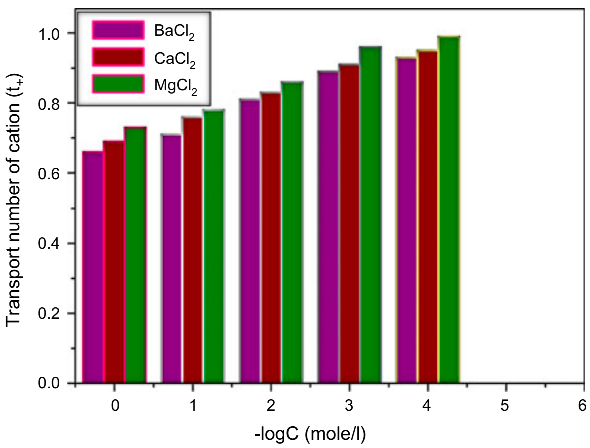

Fig. 6. The plot of transport number of cation of PVC-based NP ion-exchange composite membrane for 1:1 electrolytes ($MgCl_2$, $CaCl_2$, and $BaCl_2$) vs. concentrations.

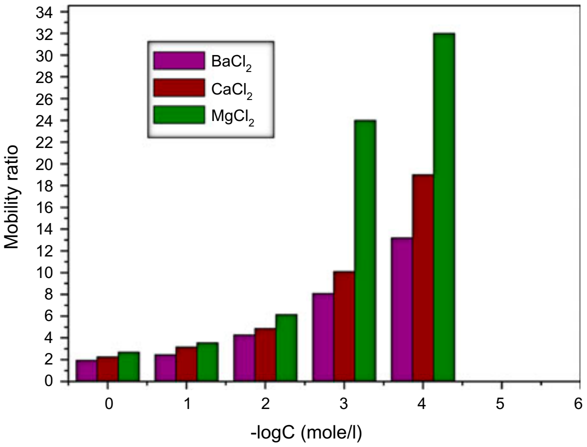

Fig. 7. The plot of mobility ratio of PVC-based NP ion-exchange composite membrane for electrolytes ($MgCl_2$, $CaCl_2$, and $BaCl_2$) vs. concentrations.

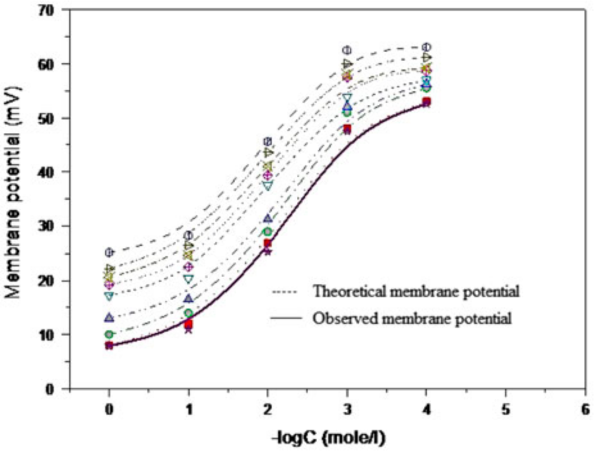

Fig. 8. Plots of membrane potential (theoretical and observed) (mV) vs. (mol/l) at different concentrations of $BaCl_2$ electrolyte solution for PVC-based NP ion-exchange composite membrane.

Table 2
The surface charge densities of PVC-based NP composite membrane

Membrane	Electrolytes	Charge density (eq/l)
PVC-based NP composite membrane	$BaCl_2$	0.77
	$CaCl_2$	0.56
	$MgCl_2$	0.48

The mobility $\bar{\omega}$ (standard error ± 0.01) of the electrolyte in the membrane phase was found to be high and follows the increasing order $BaCl_2 < CaCl_2 < MgCl_2$ as shown in Fig. 7. The high mobility is attributed to a higher transport number of comparatively free cations of electrolyte which was also found to have the like style as the mobility in low concentrated solution.

The fixed charge phenomena of TMS theory for an ion-exchange membrane is an appropriate opening point for the investigations of the real mechanisms of ionic or molecular processes which occur in membrane phase [18–21]. The membrane potential, according to the TMS method, applicable to an idealized system is represented in Eq. (2). The surface charge densities of PVC-based NP composite membrane were investigated from the membrane potential measurement and could also be determined from the transport number. To determine this parameter in the simple case of a 1:1 electrolyte and a membrane carrying various charge densities $\bar{D} \leq 1$. The theoretical membrane potential and the observed membrane potential were plotted as a function of $-\log C_2$ as shown in Fig. 8. Thus, the coinciding curve for various electrolyte systems gave the value of charge density $\bar{D}$ (Table 2) within the membrane phase. Thus, the order of charge density for electrolytes used was found to be $BaCl_2 > CaCl_2 > MgCl_2$.

4. Conclusions

It is clear from the above discussion; the addition of inorganic material (NP) into the organic polymer (PVC) improves the thermal, mechanical and chemical stability. The enhancement in these properties is due to the collective effect of both PVC and NP, which are usually bound together with smart chemistry and ionic interactions. The electro active material NP is responsible for the transport of ions because of the presence of negatively charged phosphate (PO_4^{2-}) group. However, PVC is used only as a binder for the preparation of membrane from the powder of NP and it is confirmed that the PVC doesn't contribute towards the transport phenomena. The scope of this composite ion-exchange membrane has a great application in desalination and wastewater treatment applications.

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Nomenclature

C_1, C_2 — concentrations of electrolyte solution on either side of the membrane (mol/l)
$\bar{C}_{1+}$ — cation concentration in membrane phase 1 (mole/l)
$\bar{C}_{2+}$ — cation concentration in membrane phase 2 (mole/l)
C_i — ith ion concentration of external solution (mole/l)
$\bar{C}_i$ — ith ion concentration in membrane phase (mole/l)
$\bar{D}$ — charge density in membrane (eq/l)
F — Faraday constant (C/mole)
q — charge effectiveness of the membrane
R — gas constant (J/K/mole)
t_+ — transport number of cation
t_- — transport number of anion
$\bar{u}$ — mobility of cations in the membrane phase $(m^2\ v^{-1}\ s^{-1})$
$\bar{v}$ — mobility of anions in the membrane phase $(m^2\ v^{-1}\ s^{-1})$
V_k — valency of cation
V_x — valency of fixed charge group
$\bar{U}$ — $\bar{U} = (\bar{u} - \bar{v})/(\bar{u} + \bar{v})$

Greek symbols

$\gamma_\pm$ — mean ionic activity coefficients
$\bar{\omega}$ — mobility ratio
$\Delta\psi_m$ — observed membrane potential (mV)
$\Delta\bar{\Psi}_m$ — theoretical membrane potential (mV)
$\Delta\Psi_{Don}$ — Donnan potential (mV)
$\Delta\bar{\Psi}_{diff}$ — diffusion potential (mV)

Abbreviations

IEC — ion-exchange capacity
PVC — Polyvinyl chloride
NP — Neodymium phosphate
SCE — saturated calomel electrode
SEM — scanning electron microscopy
TEM — transmission electron microscopy
TMS — Teorell, Meyer and Sievers

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