

APPLIED CHEMISTRY

Electrosynthesis of Potassium Permanganate in a Cation Exchange Membrane Cell

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Potassium permanganate is produced by the electro-oxidation of alkaline potassium manganate in a divided electrolytic cell. A filter press type flow electrolyzer has been designed, fabricated, and operated with perfluoro sulfonic acid based cation exchange membrane Nafion 417, precious metal/precious metal oxide coated titanium anode, and stainless steel cathode. Optimum process parameters are evaluated and reported. Performance characteristics of coated titanium anodes are compared with conventional nickel anodes, to fix the most suitable one for the job on hand. Anode materials have been electrochemically characterized by potentiodynamic studies in alkaline potassium manganate solution. Transport properties of the membrane Nafion 417 for K^+ ions and water molecules are studied using a small membrane cell operating on batch mode. It has been estimated that each K^+ ion transported across the membrane carries with it 1.5 to 1.7 water molecules. The anolyte contains K_2MnO_4 and KOH. Studies reveal that the relative current efficiency value for electro-oxidation of manganate and the competing anodic oxygen evolution may have a direct bearing on the source of K^+ ion transported across the cation exchange membrane.

1. Introduction

Potassium permanganate is an environmentally benign and versatile industrial oxidant. It is used for the purification of drinking water, cleaning of swimming pools, and treatment of industrial wastewater. It acts as a general oxidant, attacking all organic material, converting them into carbon dioxide and water. It reacts over a wide range of pH and requires no additional catalyst.^{1–4} In analytical chemistry, acidic solutions of permanganate are used as a chemiluminescence reagent.^{5,6} During the oxidation of organic compounds, potassium permanganate is reduced to manganese dioxide and the reduced manganese dioxide is recycled.⁷ The recycled manganese dioxide can be used as a mild oxidant, as catalysts in batteries, as pigments in paints and dyes, and as raw material for permanganate production.⁸ The recycling of manganese dioxide has made the usage of potassium permanganate environment friendly.⁷

The production of potassium permanganate is produced by the electrooxidation of potassium manganate.^{9–12} Potassium manganate is obtained by roasting a solid mixture of manganese dioxide and potassium hydroxide in air at 453–493 K. The calcined mass is dissolved in potassium hydroxide solution to get a green colored potassium manganate solution, which is electrochemically oxidized to potassium permanganate in an electrochemical cell.¹³

Studies on the electrosynthesis of potassium permanganate are very few in open literature. Freeman and Mamantov¹⁴ studied linear sweep voltammetry of permanganate and manganate in alkaline media. Galus et al.¹⁵ studied the electrode kinetics of manganate/permanganate system on a variety of anode materials by cyclic voltametric technique. Pletcher et al.¹⁶ have studied the mechanism and kinetics of the MnO_4^-/MnO_4^{2-} couple at nickel electrodes in $2.5 \text{ mol} \cdot \text{dm}^{-3}$ potassium hydroxide.

Nowadays, membranes are being used as efficient tool for the separation of liquid mixtures or gases in the chemical and

biomedical industry, in water desalination, and in wastewater purification. In the chlor alkali industry, conventional mercury–amalgam cells and diaphragm cells have given way to environmentally friendly and energy conserving membrane cells. Use of perfluoro sulfonic acid membranes in fuel cells results in cell potentials, very close to thermodynamic equilibrium values. With the help of ion-exchange membranes, a larger pH gradient between anolyte and catholyte in an electrolytic cell could be maintained. The permselectivity and stability of ion-exchange membranes have revolutionized electrochemical reactor design engineering. Pletcher et al.¹⁶ have advocated bright prospects for industrial electrolyzers with cation exchange membranes and platinized titanium anodes.

By isolating the anolyte from the catholyte, the cationic membrane (1) permits the production and concentration of valuable potassium hydroxide in the catholyte and permits the return of that potassium hydroxide to the upstream portion of the process, (2) prohibits or at least substantially inhibits the movement of permanganate ions to the cathode to avoid conversion of permanganate to undesired manganate, (3) inhibits the potentially explosive mixing and contact of oxygen formed at the anode with hydrogen formed at the cathode, (4) permits the reduction of the distance between the cathode and the anode to permit the running of the process at reduced voltages, and hence, reduced power costs, (5) permits an increased cathode area which results in lower overvoltages required to run the process, and (6) reduces undesirable side reactions in the anolyte region because the potassium hydroxide generated in the catholyte region is kept separate from the anode.

Worldwide there is an ever increasing urge for *green* technology. As a contribution toward this goal, our group has designed a filter press electrolyzer for the production of pure $KMnO_4$. This cell uses a perfluoro sulfonic acid based cation exchange membrane, Nafion 417, for separating potassium manganate/permanganate solution in the anode chamber and KOH solution in the cathode chamber. A precious metal/

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Permanganate Membrane Cell

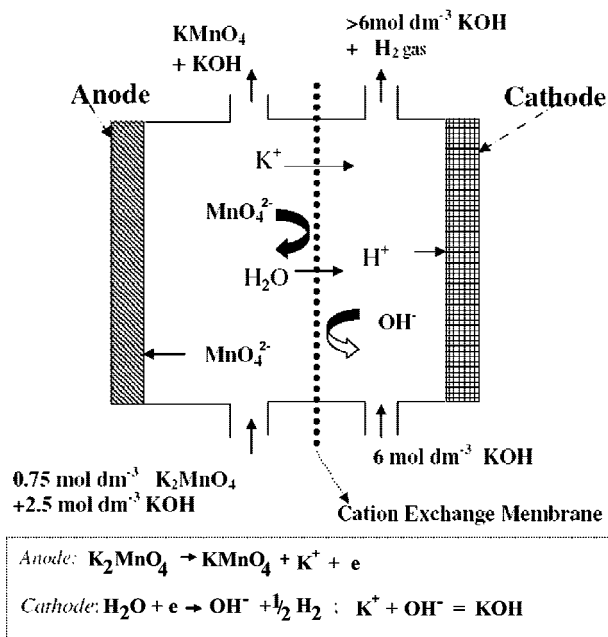


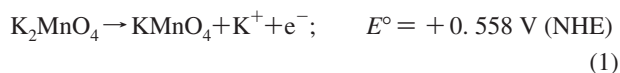
Figure 1. Principle of ion exchange membrane electrochemical process for potassium permanganate preparation.

precious metal oxide coated titanium anode and a stainless steel cathode are used. Performance characteristics of coated titanium anodes are compared with conventional nickel anodes. The electrolyzer has been operated on batch as well as flow mode. Water and K^+ transport properties of membrane and potentiodynamic as well as voltammetric behavior of the anode materials in alkaline potassium manganate solutions have been studied. Optimum process parameters required for scaling up the process to the industrial level are reported.

2. Theory

In a cation exchange membrane cell, oxidation and reduction reactions take place at anode and cathode compartments, respectively. The membrane prevents the anode and cathode products from mixing together. Alkaline potassium manganate is fed to the anode compartment and alkali solution is fed to the cathode compartment. On the application of the electric field, the oxidation of manganate to permanganate takes place along with the parasitic oxygen evolution at the anode. The reduction of water takes place with the liberation of hydrogen gas and formation of hydroxyl ions at the cathode. In the presence of electric field, K^+ ions from the anode compartment diffuse through membrane to the cathode compartment along with associated water molecules and form KOH by combining with hydroxyl ions formed there. The principle of the permanganate membrane cell is illustrated in Figure 1. K^+ ions, transported from the anode to cathode chamber may be from K_2MnO_4 and KOH. The amount of K^+ transported from K_2MnO_4 and KOH is decided by the current efficiency of manganate oxidation and the oxygen evolution side reaction. In the anode chamber, K_2MnO_4 exists as K^+ and MnO_4^{2-} ions. MnO_4^{2-} is oxidized to MnO_4^- . Cation exchange membrane selectively allows the transport of K^+ ions from the anode chamber to the cathode chamber along with associated water molecules. The electrochemical reactions occurring in the cell are given below:¹³

Anode: MnO_4^{2-} ions are oxidized to MnO_4^- ¹⁷



Cathode: Water is discharged to form hydrogen gas and hydroxyl ion

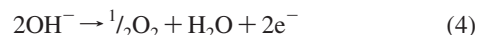


OH^- ions combine with the K^+ ion from K_2MnO_4 transported through the membrane to form KOH.



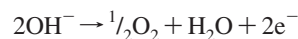
The overall equilibrium cell voltage is -1.387 V . A 1 mol portion of K^+ from K_2MnO_4 is transported for 1 mol of $KMnO_4$ production.

When the anolyte pH is more than 12, ($E_{O_2} = +0.518 \text{ V}$), the oxygen evolution side reaction occurs along with manganate oxidation.



The theoretical potential for parasitic oxygen evolution is evaluated as follows.

The pH varies with the alkali concentration, and the potential varies with pH. The values are calculated using Nernst law.¹⁸ The Nernst equation for oxygen evolution reaction is



$$E_{O_2} = E^\circ + (0.059/n) \log p_{O_2}/[a_{OH^-}]^2 = 0.401 + 0.059pOH \quad (5)$$

$$pOH = 14 - pH \quad (6)$$

if pH is 12, $E_{O_2} = +0.518 \text{ V}$, and if pH is 14, $E_{O_2} = +0.401 \text{ V}$ (NHE) (" E° " is the standard potential, $E^\circ = 0.401 \text{ V}$ for oxygen evolution, and " E_{O_2} " is the equilibrium potential).

K^+ from KOH present in the anolyte passes to the cathode chamber to form KOH at the cathode chamber. The overall equilibrium cell voltage [eqs 2 and 4] for the parasitic reaction is -1.23 V .

The current efficiency for the manganate oxidation and oxygen evolution depends upon the choice of anode material. If the anode material possesses higher oxygen overvoltage and lower overvoltage for manganate oxidation, then the electrochemical process for permanganate production will be the preferred one.

3. Experimental Section

3.1. Anodes. Precious Metal or Mixed Metal Oxide Film Coated Titanium Anodes. Platinum film coated titanium, RuO_2 coated titanium, and IrO_2 mixed with 5 mol % Pt coated titanium have been prepared by thermal decomposition technique.^{19,20} Platinum or other metallic chlorides are dissolved in isopropyl alcohol and the solution is brushed onto pretreated titanium substrate, layer by layer. After brushing of each layer the titanium substrate is baked in a electrically preheated furnace at 700 K in presence of air. The process is continued until the required film thickness is obtained on the substrate. Film thicknesses of 2 and 5 μm are obtained for platinum and other oxides respectively.

Nickel. Plain nickel sheet and 4-fold of woven nickel mesh are used. For voltammetric studies, anodes used are sheets and have a dimension of 1 cm \times 17 cm. For water transport studies, anodes are made from expanded titanium mesh of dimension 5 cm \times 5 cm; four such anodes are bundled together and used. For the filter press type flow electrolyzer, anodes are made from woven nickel mesh or expanded titanium mesh of dimension 9 cm \times 25 cm; four such anodes are bundled together and used.

3.2. Cathode. Expanded stainless steel mesh is used for all studies.

3.3. Membrane. Nafion 417 perfluoro sulfonic acid based cation exchange membrane supplied by DuPont Inc. (equiv wt 1100, reinforced with PTFE, thickness 0.017 in.) is used in all studies. The membrane is shipped in H^+ form by the supplier. It has to be kept dipped in 1% aqueous KOH solution for 12 h to convert it to K^+ form.

3.4. Cells. Potentiodynamic studies have been carried out in a standard H-type glass cell. Platinum foil is the counter electrode. All potentials are measured with respect to a saturated calomel electrode (SCE) and reported with respect to a standard hydrogen electrode (SHE). Voltammograms are recorded using Solartron SI 1287A electrochemical interface.

A two compartment cell, made of Perspex material, having anode and cathode compartments of dimensions $5\text{ cm} \times 6\text{ cm} \times 5\text{ cm}$, separated by a Nafion 417 membrane is used for water transport studies. An Aplad digital regulated DC power supply; 0–10 A and four 1/2 digit digital multimeters are used for these studies. In both voltammetric and water transport studies, the temperature was maintained at $300 \pm 2\text{ K}$ by a thermostat.

Filter press electrolyzer is fabricated from solid polypropylene materials. The membrane and electrodes are fitted in a leak proof manner, using EPDM (ethylene propylene diene poly methylene) gaskets. The anode and cathode chambers have a cavity of size $9\text{ cm} \times 25\text{ cm} \times 1.5\text{ cm}$ at their center, for holding the electrolyte. The effective size of the anode chamber fitted with 4-fold expanded mesh anode was $9\text{ cm} \times 25\text{ cm} \times 1\text{ cm}$ only. Studies are made by varying the concentrations KOH solution and potassium manganate. The catholyte is an aqueous KOH solution. The chambers are fed continuously with the respective electrolytes, in countercurrent mode. The cell is operated at 323 K, and the bath is steam heated.

3.5. Chemicals. K_2MnO_4 is prepared in bulk quantities, by fusing the laboratory grade MnO_2 and KOH by the method developed by Reides and Carus.^{21,22} Manganese dioxide is added to molten potassium hydroxide (70–80%) in a reactor to get a 1:5 molar ratio of MnO_2 and KOH. Air is passed into the mixer with help of a sparging device. The temperature is maintained in the range of 523–593 K. The reaction mixture remains fluid during entire time of 3 h. On cooling, it becomes solid. It is scrapped and ground to a powder and then roasted at 523 K for 1 h. The roasted powder is treated with 10–12% KOH until the overall concentration of KOH is about 450–550 $g\text{ L}^{-1}$. Upon cooling to 303 K, the K_2MnO_4 settles and is separated by centrifugation for use in the preparation of electrolyte.

KOH and MnO_2 used are Reidel make laboratory grade chemicals, and all other reagents are analar grade E Merck make. Double distilled water is used for fundamental studies, and distilled water is used for preparative electrolysis.

3.6. Analysis. Potassium manganate synthesized in these studies is estimated by UV spectrum (5000 UV-vis-NIR spectrometer Varian) at 608 nm and counter checked by atomic absorption spectroscopy (AAS, SectrAA 220, Varian MAG) The concentrations of permanganate and manganate in the anolyte liquor of the cell are determined by UV spectra at 526 and 608 nm, respectively.

4. Results and Discussions

4.1. Potentiodynamic Studies. The potentiodynamic behavior of the anode materials is studied in 2.5 mol dm^{-3} KOH and 1.0 mol dm^{-3} potassium manganate solutions in the potential range of 0.24 to 0.84 V (SHE) at a scan rate of 1 mV s^{-1} at 300 K. Potentiodynamic curves are shown in Figures 2 and 3.

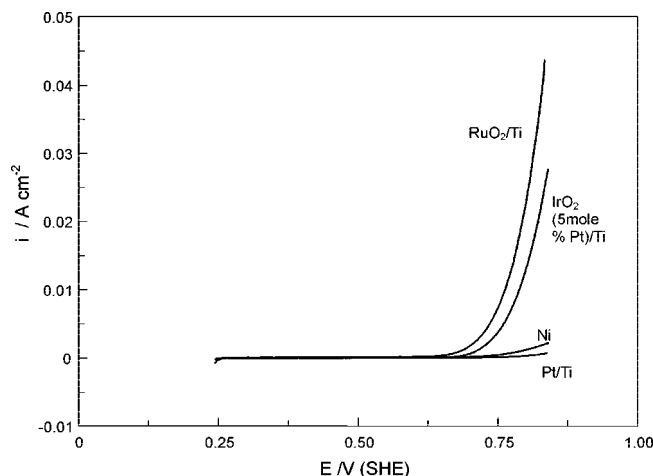


Figure 2. Potentiodynamic curves for RuO_2/Ti , IrO_2 (5 mol % Pt)/Ti, nickel, and platinumized titanium anodes in 2.5 mol dm^{-3} KOH solution; potential range 0.24–0.84 V (SHE); scan rate 1 mV s^{-1} ; $T\ 300\text{ K}$.

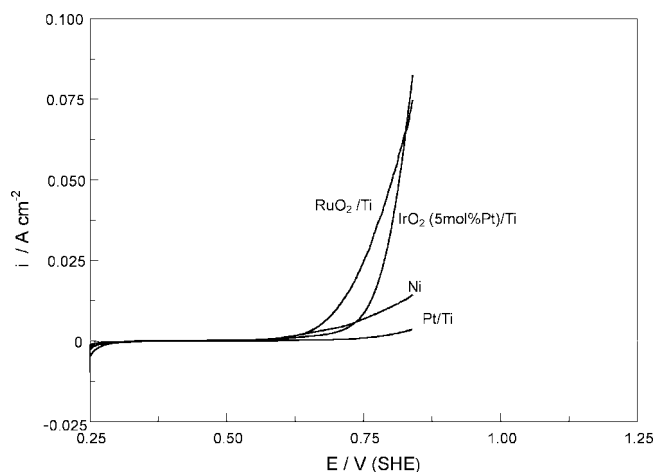
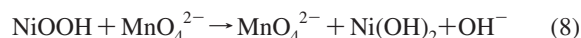


Figure 3. Potentiodynamic curves for RuO_2/Ti , IrO_2 (5 mol % Pt)/Ti, nickel, and platinumized titanium anodes in 2.5 mol dm^{-3} KOH + 1 mol dm^{-3} K_2MnO_4 solution; potential range 0.24–0.84 V (SHE); scan rate 1 mV s^{-1} ; $T\ 300\text{ K}$.

They indicate that oxygen evolution starts at 0.64 V. In the case of RuO_2 and 5 mol % Pt doped IrO_2 anodes, the oxygen evolution reaction competes with the manganate oxidation reaction. For nickel and platinum film anodes, the oxygen reaction is taking place at a potential above 0.84 V in pure 2.5 mol dm^{-3} KOH solution (Figure 2). In alkaline K_2MnO_4 solutions, the curve is shifted toward the negative side and there is increase of current in the manganate oxidation potential range of 0.56–0.64 V. The potentiodynamic behavior of RuO_2 , 5 mol % Pt doped IrO_2 , and platinum film obtained in KOH are more or less similar to that obtained in alkaline manganate solutions. But the nickel anode behaves differently in alkaline manganate solutions (Figure 3) which may be attributed to manganate oxidation to permanganate via surface formed species of $Ni(OH)_2$.¹⁶



The potentiodynamic studies serve as an indicator to compare the performance of the anode materials studied for manganate oxidation. On the basis of these studies, we conclude that the titanium anodes coated with RuO_2 and 5 mol % Pt doped IrO_2

anodes are not suitable for oxidation of manganate, as oxygen evolution is the more favored reaction. In the case of nickel and platinized titanium anodes, oxygen evolution is minimal and hence they are suitable for manganate oxidation reaction. From Figure 3, it is observed that nickel anode functions efficiently at low current densities only; on the other hand, platinized titanium anode functions more efficiently at high current densities. So we used platinized titanium anode for evaluating K^+ and water transport and also for the optimization of process parameters of filter press type permanganate membrane cell.

4.2. Transport Properties of the Membrane for K^+ and Water Molecules. In the presence of electric field, alkali metal cation along with water molecules are transported through cation exchange membrane from the anode to the cathode chamber. The transport phenomenon of alkali metal ions and water across the membrane from anode to cathode compartments were studied in a chlor alkali membrane cell by Burkhardt²³ and Yeager and Malinsky²⁴ using Na^{24} and Na^{22} radioactive isotopes respectively. We do not have facilities to carry out experiments with radioactive species, but experiments are carried out using the principle of mass balance. Amount of water transported per mole of alkali metal ions depends on the concentration of alkali metal ions in the anode chamber.²⁵ The K^+ transported from the anolyte may be from K_2MnO_4 or KOH or from both. It depends upon the ratio of current efficiency of manganate oxidation and oxygen evolution.

A small filter press type cell of electrode area 25 cm^2 has been designed with Nafion 417 cation exchange membrane, platinized titanium anode, and stainless cathode. By varying the ratio of potassium manganate and KOH in the anolyte, the water molecules transported with K^+ ions across the membrane and the origin of K^+ transported are evaluated.

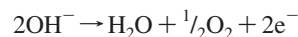
K_2MnO_4 exists as $K^+K^+MnO_4^{2-}$ in alkaline solution, and the total concentration of free K^+ is the sum of numerical values of KOH and twice the value of K_2MnO_4 in moles. The effect of the concentration of K^+ in the anolyte on the number of water molecules transported to cathode compartment along with each K^+ is studied. Studies are also conducted with anolyte containing pure 2.5 mol dm^{-3} KOH at different current densities for constant charge of 0.5 A h at 300 K . The amount of water transported per K^+ is determined. Before and after the completion of each experiment, the anolyte and catholyte volumes and their weights are noted down. Catholyte is analyzed for the amount of water and KOH and anolyte is analyzed for the amount of K_2MnO_4 and KOH before and after the experiment. Current efficiency for the $KMnO_4$ formation is determined from the amount of $KMnO_4$ formed and oxygen evolution. The cathode current efficiency is determined by analyzing KOH formed at the cathode.

The anode and cathode compartments are kept airtight. The water vapor in the anode and cathode gases is condensed by cooling to 300 K using a water jacket. The condensate is returned to the respective compartments. The anode compartment contains $K_2MnO_4 + KMnO_4 + KOH + H_2O$. The current applied to this system can be consumed only for $KMnO_4$ oxidation and O_2 evolution. Current efficiency for oxygen evolution reaction (OER) is obtained by subtracting the CE for $KMnO_4$ formation from 100.

4.2.1. After the Electrolysis. Anode Compartment. If there is only $KMnO_4$ formation, KOH concentration will be constant. Loss of water is due its migration to the cathode side along with K^+ ions. If there is oxygen evolution, then, there will be loss of KOH. Water balance for the process as a whole should

include H_2O formed due to OER, H_2O vapor carried out along with O_2 gas, and H_2O transported with K^+ ion.

OER in alkaline solutions:



For the passage of current of 1 Faraday, 0.25 mol of oxygen gas and 0.5 mol of water will be produced.

In the present system, the total water formed during oxygen evolution

$$\frac{\%CE \text{ of OER} \times 0.5 \text{ mol}}{100} = B \text{ mol} \quad (9)$$

Part of this water is carried away by the liberated gas.

As the gases are cooled to 300 K and the condensed water is returned to the respective compartments, the gases will be saturated at 300 K .

The vapor pressure of water at 300 K is 26.739 mm Hg .²⁶ The vapor content of the gas liberated can be found as follows:

partial pressure ratio \equiv mole ratio

$$\frac{\text{partial pressure of vapor}}{\text{partial pressure of gas}} = \frac{\text{moles of vapor}}{\text{moles of gas}} \quad (10)$$

At 300 K , the partial pressure of water is 26.739 mmHg

$$\text{partial pressure ratio} = \frac{26.739}{760 - 26.739} = \frac{0.0365}{1} \quad (11)$$

A 1 mol portion of O_2 at 300 K will carry with it 0.0365 mol of water vapor.

Total amount of water vapor carried out by O_2 for 1 F current:

$$\frac{\%CE \text{ for OER} \times 0.0365 \times 0.25}{100} = C \text{ mol} \quad (12)$$

In the presence of an electric field, for 1 F, 1 mol of K^+ ion migrates to the cathode compartment along with associated water molecules.

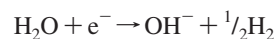
Water transported along with

$$1 \text{ mol } K^+ = D_{\text{anode}} \text{ mol} = [A - B + C] \text{ mol} \quad (13)$$

where A is the difference in the amount of water in the anolyte feed and the anolyte effluent.

Cathode Compartment. The amount of KOH formed at the cathode compartment is independent of anodic reactions. Gain of water is due its migration to the cathode side along with K^+ ions. Since there is hydrogen evolution reaction (HER), then, there will be loss of H_2O due to its decomposition. Water balance for the process as a whole should include water utilized for HER, H_2O vapor carried out along with H_2 gas, and H_2O transported with K^+ ion to cathode compartment.

HER in alkaline solutions:



For the passage of current of 1 F, 0.5 mol of hydrogen gas is formed, and 1 mol of water is decomposed. In the present system, the total water decomposed during hydrogen evolution

$$\frac{\%CE \text{ of HER} \times 1 \text{ mol}}{100} = E \text{ mol} \quad (14)$$

Part of this water is carried away by the liberated gas.

As the gases are cooled to 300 K and the condensed water is returned to the respective compartments, the gases will be saturated at 300 K .

Table 1. Transport Properties of the Nafion 417 Membrane in Permanganate Electrolyzer^a at 300 K

KOH/mol	K ₂ MnO ₄ /mol	total K ⁺ /mol	amount of H ₂ O transported per mole of K ⁺ transported/mol
2.00	0.50	3.00	1.70
2.50	0.375	3.25	1.60
2.50	0.00	2.50	1.71
2.125	0.375	2.875	1.62
2.50	0.50	3.50	1.59
2.50	0.625	3.75	1.58
2.50	0.75	4.00	1.58
2.50	0.875	4.25	1.55
2.50	1.00	4.50	1.52

^a Electrolysis conditions: cathode stainless steel, anode platinized Ti, membrane Nafion 417 cation exchange, interelectrode gap 0.4 cm, electrode area 5 cm × 5 cm: 25 cm², current density 5, 20, and 50 mA cm⁻², total charge 0.50 A h, anolyte 0.375–1 mol dm⁻³ K₂MnO₄ + 2–2.5 mol dm⁻³ KOH with total K⁺ concentration >2.5 mol dm⁻³ (volume 120 cm³), catholyte 6.0 mol dm⁻³ KOH (volume 120 cm³), process type batch process (electrolyte is not flowed).

The vapor pressure of water at 300 K is 26.739 mmHg.²⁶ A 1 mol portion of H₂ at 300 K will carry with it 0.0365 mol of water vapor.

Total amount of water vapor carried out by H₂ for 1 F current:

$$\frac{\%CE \text{ for HER} \times 0.0365 \times 0.5}{100} = F \text{ mol} \quad (15)$$

In the presence of electric field, for 1F, 1 mol K⁺ ions migrate to the cathode compartment along with associated water molecules.

Water is transported along with

$$1 \text{ mol K}^+ = D_{\text{cathode}} \text{ mol} = [G - E - F] \text{ mol} \quad (16)$$

where *G* is the difference in the amount of water in the catholyte feed and the catholyte effluent.

In all the experiments, the cathode current efficiency is determined to be 97 ± 2%. Water transported across the membrane along with K⁺ are in the range of 1.5–1.7 molecules of H₂O per K⁺. Results are reported in Table 1.

Table 2 gives the results regarding K⁺ ions transported under various operating conditions. It is observed that if current efficiency for the electro-oxidation of manganate is about 98–100%, there is no change in the KOH concentration in the anolyte. This indicates that K⁺ ions transported across the membrane are only from K₂MnO₄. When the current efficiency for the electro-oxidation of manganate is less than 90%, there is a decrease in KOH concentration in the anolyte, due to the oxygen evolution. So, the origin of K⁺ ions in this case is K₂MnO₄ and KOH in the anode chamber.

4.3. Operation of Filter Press Type Membrane Cell for Potassium Permanganate Production. Expanded stainless steel mesh of area 225 cm² is used as the cathode. Platinized titanium expanded mesh or expanded nickel or RuO₂ coated expanded titanium mesh or 5 mol % Pt doped IrO₂ coated expanded titanium mesh of area 900 cm² is used as anode. Anolyte containing 0.75 mol dm⁻³ of potassium manganate and 2.5 mol dm⁻³ KOH and catholyte containing 6 mol dm⁻³ KOH are continuously fed to the anode and cathode chambers respectively. The cell is operated at 323 K. Anolyte and catholyte are fed in countercurrent mode. Process parameter optimization studies have been done only for platinum coated titanium mesh anode. Under similar conditions of anolyte flow and current density, current efficiency studies have been carried out using nickel, RuO₂, and IrO₂ anodes for the sake of comparison.

4.3.1. Effect of Anolyte Flow Rate on Current Efficiency. The flow rate of anolyte is varied and the current efficiency for permanganate formation is determined at a constant charge of 10 A h per experiment. Figure 4 shows the effect of anolyte flow on the current efficiency for the formation of potassium permanganate at various current densities. In general, at all current densities, the current efficiency increases with increase in anolyte flow rate. An increase in flow rate leads to increase in the activity of the reactant at the anode surface. The increase in flow of anolyte forces the product permanganate to diffuse away from the anode to pave the way for more manganate ions at the anode surface. At 2 mA cm⁻², the current efficiency increases with an increase in the flow rate and reaches a maximum current efficiency of 98% at a flow rate of 6 × 10⁻³ dm³ min⁻¹. At the higher current density of 50 mA cm⁻² and at a lower flow rate of 2 × 10⁻³ dm³ min⁻¹, very low current efficiency (10%) is observed. At the flow rate of 20 × 10⁻³ dm³ min⁻¹, an optimum current efficiency value of 75% is obtained at a current density of 30 mA cm⁻².

4.3.2. Influence of Anolyte Flow Rate on the Concentration of Permanganate. Figure 5 shows the effect of anolyte flow rate on the concentration of permanganate at a constant electrolysis time of 1 h. It is observed that the permanganate concentration increases with an increase in flow rate but decreases with an increase in current density. A maximum permanganate concentration of 55 g L⁻¹ is achieved at 5 and 10 mA cm⁻² even at low flow rates. At 50 mA cm⁻², the permanganate concentration increases from 5 to 30 g L⁻¹ with flow rate. The critical concentration of KMnO₄ in the mother liquor⁹ for the crystallization is around 45 g L⁻¹. When the mother liquor with KMnO₄ (<45 g L⁻¹) is cooled and crystallized, 30 g L⁻¹ of KMnO₄ is retained in the mother liquor.⁹

4.3.3. Variation of Current Efficiency with Current Density. Figure 6 describes the effect of current density on current efficiency for permanganate formation at a constant charge of 10 A h. The current efficiency decreases with increase in current density at all flow rates. A maximum value of 90–95% is achieved at current densities lesser than 15 mA cm⁻² at all flow rates, and an optimum current efficiency of 70% could be achieved if the electrolyzer is operated in the flow rate range of 15–20 × 10⁻³ dm³ min⁻¹.

4.3.4. Effect of Anode Materials. The electrolyzer is operated with various anode materials with anolyte feed of 0.75 mol dm⁻³ of K₂MnO₄ and 2.5 mol dm⁻³ KOH and catholyte feed of 6 mol dm⁻³ KOH, at 20 mA cm⁻² for a total charge of 2.22 Ah, at an anolyte flow rate of 8 × 10⁻³ dm³ min⁻¹, at 323 K. Table 3 gives the results of the performance comparison studies.

Two competing reactions, namely permanganate oxidation and water electrolysis occur in the cell. The total current passed is shared between these two reactions depending on electro-catalytic properties of anode materials. The cell voltage values of anode materials reflect on the type of reaction occurring in the electrolyzer. RuO₂ and IrO₂ anodes exhibit very low values of current efficiency (20–30%) for manganate oxidation. This is due to the lower oxygen over voltage of these electrodes and the predominant electrode reaction is oxygen evolution. Nickel exhibits a current efficiency of 60% for manganate oxidation, while that on platinum is 80%. This is due to their higher oxygen overvoltage on platinum. So, it is inferred that the use of RuO₂ and IrO₂ anodes for the electrochemical production of permanganate is not advisable. The platinized titanium anode is the most suited anode material.

Table 2. Relationship with the CE and the Origin of K^+ Transported in Membrane Permanganate Electrolyzer^a

anolyte composition	$i/\text{mA cm}^{-2}$	CE for K_2MnO_4 oxidation/%	water transport per K^+ /mol	origin of K^+ transported
1 mol dm^{-3} K_2MnO_4 + 2.5 mol dm^{-3} KOH	5	98	1.6	K_2MnO_4 (100%)
1 mol dm^{-3} K_2MnO_4 + 2.5 mol dm^{-3} KOH	30	75	1.6	K_2MnO_4 (75%) and KOH (25%)
1 mol dm^{-3} K_2MnO_4 + 2.5 mol dm^{-3} KOH	50	45	1.6	K_2MnO_4 (45%) and KOH (55%)

^a Electrolysis conditions are as mentioned in Table 1.

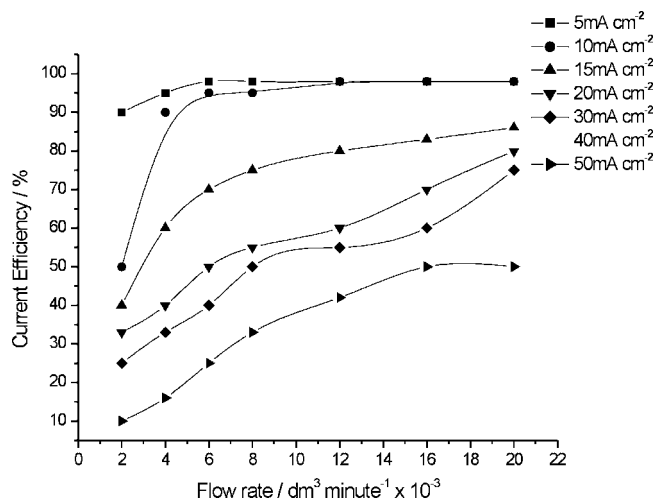


Figure 4. Variation of current efficiency with respect to the flow rate of anolyte ($0.75 \text{ mol dm}^{-3} K_2MnO_4 + 2.5 \text{ mol dm}^{-3} KOH$) feed, at constant current densities from 5 to 50 mA cm^{-2} in the Nafion 417 cation ion exchange membrane fitted permanganate electrolyzer: T 323 K; charge 10.0 A h.

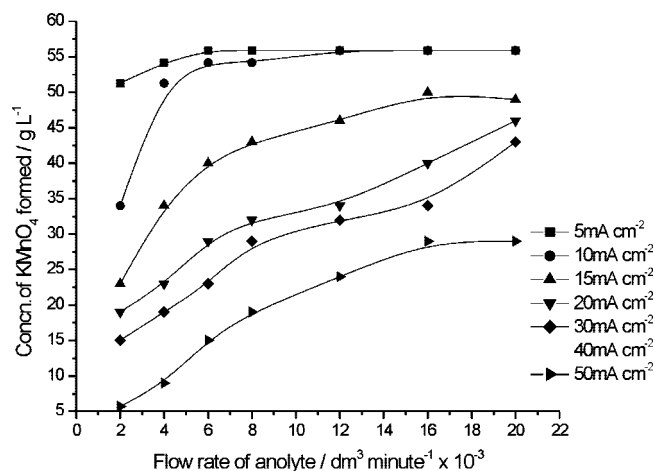


Figure 5. Effect of anolyte ($0.75 \text{ mol dm}^{-3} K_2MnO_4 + 2.5 \text{ mol dm}^{-3} KOH$) flow rate on the concentration of $KMnO_4$ formation at constant current densities from 5 to 50 mA cm^{-2} in the Nafion 417 cation ion exchange membrane fitted permanganate electrolyzer: T 323 K; electrolysis time 1 h.

5. Conclusions

Anode materials, namely, nickel as well as platinum, RuO_2 , and IrO_2 film coated titanium anodes have been prepared. Their suitability for manganate oxidation has been evaluated by cyclic voltammetric and potentiodynamic studies. Transport studies of K^+ and water have been carried in permanganate membrane electrolyzer and it is observed that 1.5–1.7 molecules of water is transported for every K^+ ion. It has been proved that K^+ transported from the anode chamber may be from K_2MnO_4 or KOH or from both depending upon the relative current efficiencies for permanganate formation and oxygen formation.

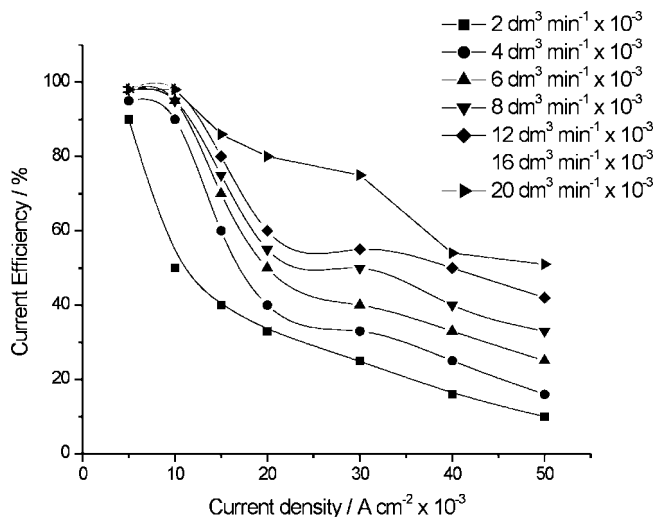


Figure 6. Effect of current density on current efficiency at constant flow rate of anolyte ($0.75 \text{ mol dm}^{-3} K_2MnO_4 + 2.5 \text{ mol dm}^{-3} KOH$) feed $2\text{--}20 \times 10^{-3} \text{ dm}^3 \text{ min}^{-1}$ in the Nafion 417 cation ion exchange membrane fitted permanganate electrolyzer: T 323 K; charge 10.0 A h.

Table 3. Comparative Performance Data of Anode Materials in Electrochemical Production of Potassium Permanganate^a

anode material	average cell voltage/V	current efficiency (CE)/%
RuO_2/Ti	2.80	20
IrO_2 (5 mol % Pt)/Ti	2.80	30
nickel	3.00	60
platinized Ti	3.20	80

^a Anolyte $0.75 \text{ mol dm}^{-3} K_2MnO_4 + 2.5 \text{ mol dm}^{-3} KOH$, catholyte $6 \text{ mol dm}^{-3} KOH$, anolyte flow $8 \times 10^{-3} \text{ dm}^3 \text{ min}^{-1}$, cathode stainless steel (area $9 \text{ cm} \times 25 \text{ cm} = 225 \text{ cm}^2$), Nafion 417 cation exchange membrane, interelectrode gap 0.4 cm, cathodic current density 20 mA cm^{-2} , total charge 2.22 A h, T 323 K.

A filter press electrolyzer of electrode area $9 \text{ cm} \times 25 \text{ cm}$ has been designed and fabricated with insoluble anodes and stainless cathode with Nafion 417 cation exchange perfluoro sulfonic acid membrane. The cell has been operated for potassium manganate oxidation at different anolyte flow rates and current densities. Process parameters such as anolyte flow and current density have been optimized for a platinum anode fitted cell. Studies on the effect of anode materials on the performance of a filter press electrolyzer revealed that platinized titanium is the most suited anode material.

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