



An alternative approach to selective sea water oxidation for hydrogen production

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ABSTRACT

Sea water electrolysis is one of the promising ways to produce hydrogen since it is available in plentiful supply on the earth. However, in sea water electrolysis toxic chlorine evolution is the preferred reaction over oxygen evolution at the anode. In this work, research has been focused on the development of electrode materials with a high selectivity for oxygen evolution over chlorine evolution. Selective oxidation in sea water electrolysis has been demonstrated by using a cation-selective polymer. We have used a perm-selective membrane (Nafion®), which electrostatically repels chloride ions (Cl⁻) to the electrode surface and thereby enhances oxygen evolution at the anode. The efficiency and behaviour of the electrode have been characterized by means of anode current efficiency and polarization studies. The surface morphology of the electrode has been characterized by using a scanning electron microscope (SEM). The results suggest that nearly 100% oxygen evolution efficiency could be achieved when using an IrO₂/Ti electrode surface-modified by a perm-selective polymer.

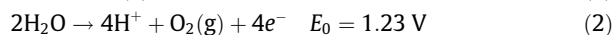
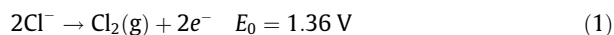
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1. Introduction

Meeting current energy requirements while satisfying environmental concerns demands new ideas for providing environmentally friendly and sustainable energy sources that can take the place of fossil fuels. Though fossil fuels will remain the most vital energy source and their supply is adequate now, once fossil fuel resources become fatally exhausted, alternative means of energy production will have to be identified without delay. Hydrogen as an energy carrier is a most appealing option, because when it is utilized (either in fuel cells or IC engines) the only by-product generated is water. Besides, hydrogen is available in both renewable (water) and non-renewable (fossil fuel) forms. However, the existing hydrogen production from non-renewable sources is inadequate to sustain its extensive use for energy purposes. Hence, cost-effective generation of hydrogen from renewable sources is essential for the so-called hydrogen economy. While hydrogen can be produced by several methods, water splitting is the most promising and clean mode of producing hydrogen as a fuel [1,2], since renewable energy (solar, wind, geothermal, etc.) can be utilized. Water electrolysis can be classified based on whether the electrolyte is alkaline, a proton-exchange membrane (PEM), or a solid-oxide electrolyte [3–5]. Alkaline electrolysis is a well-established method for producing hydrogen, while PEM electrolysis is

less common and normally utilizes expensive materials such as noble metal catalysts and sulfonated polymers as electrolytes. Solid-oxide membrane electrolysis is operated at elevated temperatures, and it is too premature to compare it with other systems. In addition to the above methods, sea water electrolysis is one of the most promising ways to produce hydrogen since it is available in plentiful supply on the Earth. However, in sea water electrolysis, toxic chlorine evolution is the preferred reaction over oxygen evolution at the anode for the following reasons:

- (i) The pH at the electrode surface becomes acidic during electrolysis, which favours chlorine evolution as it is independent of pH.
- (ii) Although oxygen evolution should be the preferred reaction over chlorine evolution according to the thermodynamic potentials [6] (Eqs. (1) and (2)), this is only valid at zero current



- (iii) The oxygen evolution reaction is associated with a higher overpotential than the chlorine evolution reaction.

Nevertheless, oxygen evolution dominates under certain conditions [7], which may be summarized as follows:

- (i) Sea water electrolysis at very low current density (<1 mA/cm²).

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- (ii) Operating the cell at far in excess of the limiting current for chlorine evolution.

However, the above two circumstances are impractical because sea water oxidation at low current density would require a very large electrode area, and electrolysis at above the limiting current would lead to IR heating and high power consumption, which would be uneconomical. Therefore, an anode material for selective oxidation of sea water to oxygen has to be developed judiciously. Bockris highlighted that sea water oxidation would seem to be the inevitable eventual source of hydrogen, and hence the necessity of finding a suitable method for eliminating chlorine evolution [8]. In view of the absence of practical oxygen evolving anodes for sea water electrolysis, a ruthenium–titanium dioxide/titanium anode, which was developed for chlorine evolution in the chloroalkali industry, is currently used, and extremely low current density (using a large anode) is applied to mitigate chlorine evolution. Research has been focused on the development of electrode materials with high selectivity for the oxygen evolution reaction over chlorine evolution. Manganese dioxide-coated IrO_2 anodes for sea water electrolysis that preferentially evolve oxygen over chlorine have been developed [7,9–11]. The reason for the selective oxidation of water by the manganese dioxide-coated electrode is as yet unclear. However, it appears that the MnO_2 film may act as a diffusion barrier layer for chloride ions. Therefore, we speculated that if we could prevent chloride anions from accessing the electrode surface by electrostatic repulsive forces, this might be effective in enhancing oxygen evolution and suppressing chlorine evolution. We assumed that this might be possible by applying a cation-selective coating on the electrode surface. To the best of our knowledge, there have not hitherto been any reports based on this idea. Hence, after thinking of some cation-exchange materials, we resolved to use a perfluorosulfonic acid membrane (Nafion®) as a cation-selective layer (because of good mechanical stability) on an IrO_2 electrode.

2. Experimental

An iridium oxide-coated titanium substrate of dimensions 2.0 cm^2 was used as the anode. A previously reported [12,13] thermal decomposition method was adopted to prepare an IrO_2 coating on a titanium substrate (IrO_2/Ti). Anode performance was examined by potentiodynamic polarization using Ag/AgCl and platinum as reference and counter electrodes, respectively. Bulk electrolysis was performed in an undivided glass cell of volume 100 ml using IrO_2/Ti as the anode and a platinum gauze as the cathode in 0.5 M sodium chloride solution at 30°C and pH 8.3 for 30 min. Surface-modified IrO_2 -coated electrodes were prepared by two different methods: (i) applying Nafion 117 solution (5 w/v in 2-propanol; Dupont Inc., USA) to the IrO_2 -coated electrode and drying in air, and (ii) hot-pressing of a Nafion-117 membrane (H^+ -form) on the iridium oxide-coated electrode surface. A scanning electron microscope (SEM) was used to examine the surface morphology of the electrode materials. The oxygen evolution efficiency was determined by subtraction of the chlorine evolution efficiency from 100%, which was assessed by way of a conventional iodometric titration method.

3. Results and discussion

Fig. 1 shows the anodic polarization behaviour of bare IrO_2 and Nafion-modified IrO_2 electrodes in 0.5 M NaCl at pH 8.3 and 30°C . The IrO_2/Ti electrode shows relatively higher current density than the Nafion solution-coated (NS/ IrO_2/Ti) electrode and the Nafion membrane-coated (NM/ IrO_2/Ti) electrode, as there is no barrier

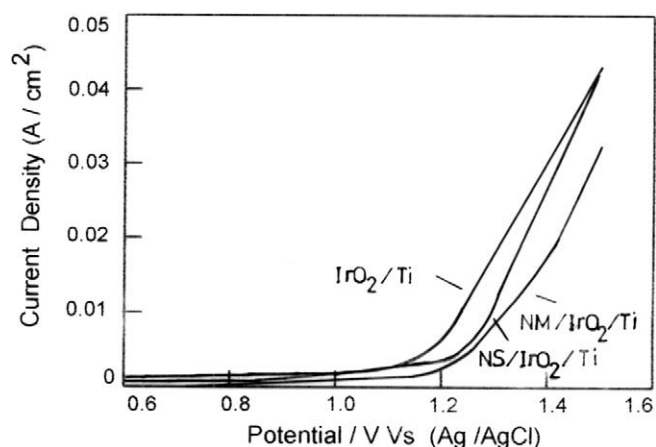


Fig. 1. Potentiodynamic anodic polarization curve of IrO_2 electrodes in 0.5 M NaCl and pH 8.3 at 30°C , Scan rate 20 mV s^{-1} , IrO_2/Ti – IrO_2 coated Ti electrode: NS/ IrO_2/Ti –Nafion solution coated IrO_2/Ti electrode: NM/ IrO_2/Ti –Nafion membrane coated IrO_2/Ti electrode.

to the evolution of either gas, i.e., O_2/Cl_2 . The current density decreased for the NS/ IrO_2/Ti electrode and further decreased for the NM/ IrO_2/Ti electrode, reflecting the resistance offered by the Nafion polymer film to gas evolution from the electrode surface. The higher current density observed for the NS/ IrO_2/Ti electrode could be attributed to the presence of micro cracks on the polymer film, which favour easy escape of gas molecules from the electrode surface, whereas in the case of the NM/ IrO_2/Ti electrode the coating is uniform (as is evident from SEM pictures), without any holes or cracks, and so offers more resistance to oxygen gas evolution.

The chlorine and oxygen evolution current efficiencies of the various electrodes in 0.5 M NaCl at pH 8.3 are shown as a function of various operating current densities in Fig. 2. The operating cell voltages at 100 mA/cm^2 are about 3.2 V higher (not illustrated) than those of conventional alkaline water electrolysis, since the conductivity of sea water is lower than that of aqueous potassium hydroxide solution. The oxygen evolution current efficiency of IrO_2/Ti is 28.7% at 100 mA/cm^2 , and on increasing the current den-

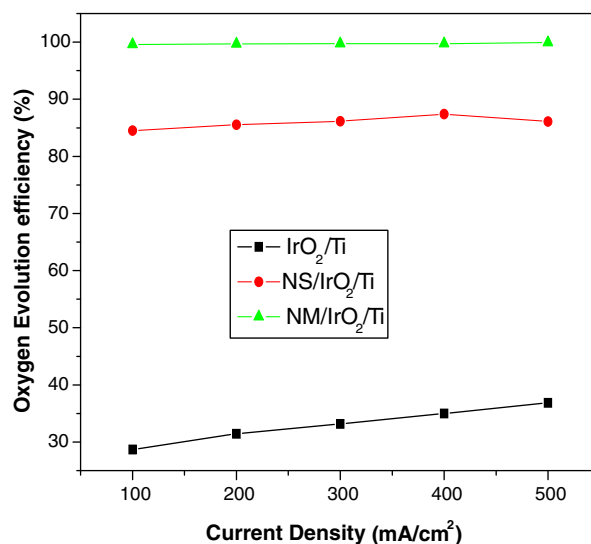


Fig. 2. Oxygen evolution current efficiency of various electrodes as a function of current density in 0.5 M NaCl and pH 8.3, at 30°C . IrO_2/Ti – IrO_2 coated Ti electrode: NS/ IrO_2/Ti –Nafion solution coated IrO_2/Ti electrode: NM/ IrO_2/Ti –Nafion membrane coated IrO_2/Ti electrode.

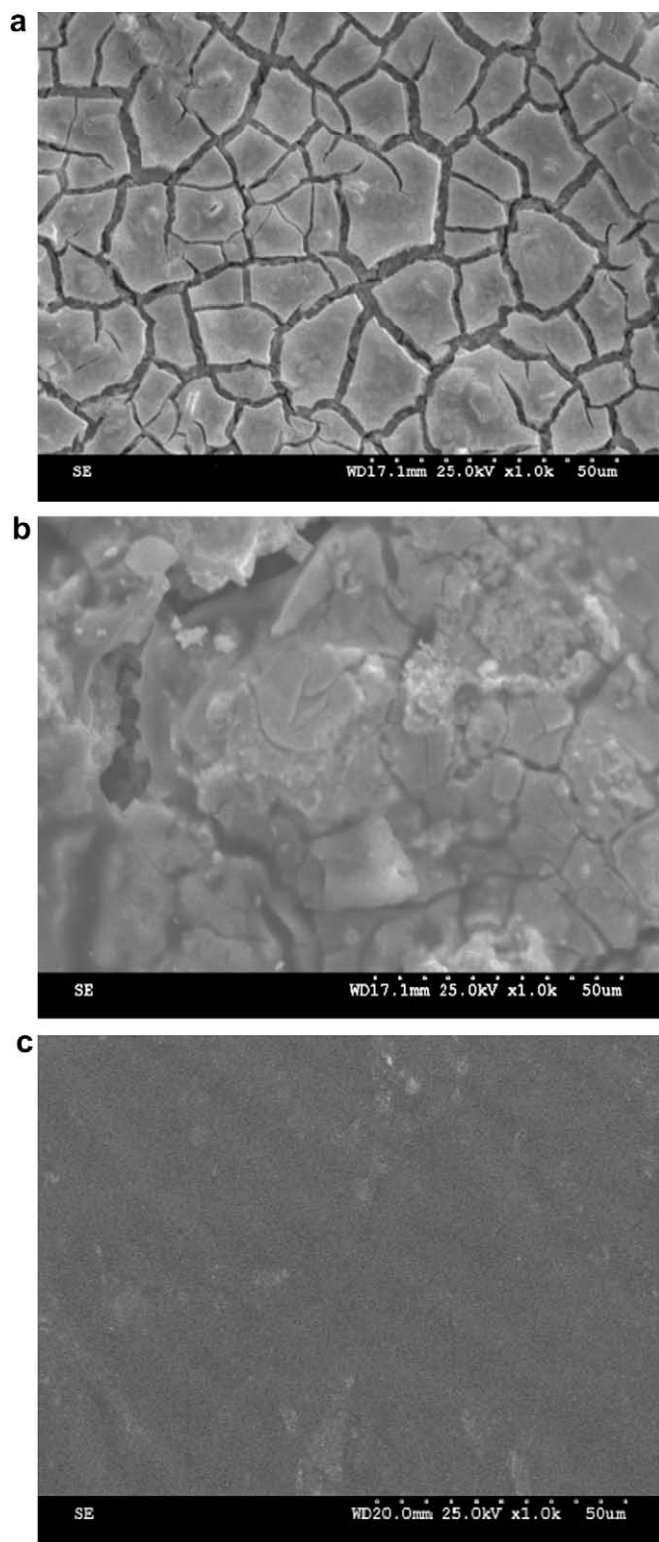


Fig. 3. SEM micrograph of surface modified IrO_2/Ti electrodes: (a) bare IrO_2 ; (b) Nafion solution coated/ IrO_2/Ti and (c) Nafion membrane coated/ IrO_2/Ti .

sity chlorine evolution decreases and oxygen evolution increases. This may be attributed to the mass-transport limitation of chloride ion to the electrode surface at higher current density, whereas in the case of oxygen evolution there is no such limitation since water is always available for oxidation; consequently, the oxygen evolution increases. In the case of the Nafion-coated electrodes,

i.e., $\text{NS}/\text{IrO}_2/\text{Ti}$ and $\text{NM}/\text{IrO}_2/\text{Ti}$, chloride ion transport to the electrode surface is hindered by the Nafion polymer film. As a consequence, water is transported through the Nafion membrane [14] and is oxidized at the electrode surface with the evolution of oxygen. Hence, water oxidation becomes the prevailing reaction (Eq. (2)) as opposed to chloride ion oxidation (Eq. (1)). However, the oxygen evolution efficiency of the $\text{NS}/\text{IrO}_2/\text{Ti}$ electrode is considerably lower than that of the $\text{NM}/\text{IrO}_2/\text{Ti}$ electrode. This may be rationalized in terms of its surface morphological nature, as shown in Fig. 3. The surface morphology of the bare IrO_2 electrode (Fig. 3a) shows wide and deep cracks, similar to those reported in the literature [15,16], which are probably introduced due to a large shrinkage in volume that results from the decomposition of chlorine compounds during the period of thermal oxidation. In the case of the $\text{NS}/\text{IrO}_2/\text{Ti}$ electrode, micro cracks (Fig. 3b) are observed, which are formed during the casting of the Nafion solution on the electrode surface; these micro cracks allow chloride ions to reach the underlying IrO_2 electrode surface and thereby favour partial chlorine evolution along with oxygen evolution. The surface morphology of the $\text{NM}/\text{IrO}_2/\text{Ti}$ electrode (Fig. 3c) is uniform, without any voids or cracks, which facilitates only water transport to the electrode surface; this increases the oxygen evolution efficiency to nearly 100% at the anode.

4. Conclusion

In summary, selective water oxidation in sea water electrolysis has been demonstrated by using a cation-selective polymer. The role of the perm-selective membrane in producing oxygen and hydrogen instead of chlorine and hydrogen in sea water oxidation has been elucidated. We believe that this approach could be useful for producing hydrogen from sea water without harming the environment and may also contribute to making the hydrogen economy a realistic one.

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