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— Review —

**PERSPECTIVE ON ELECTROCHEMICAL ENERGY  
CONVERSION IN FUTURE**

—5th JAPAN-USSR Seminar on Electrochemistry—

By

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and A. MATSUDA\*\*\*

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**Abstract**

The 1st JAPAN-USSR Seminar on Electrochemistry was held in Tokyo in 1974 on the basis of the mutual agreement between the Japan Electrochemical Society and the Academy of Sciences of the USSR for the promotion of the scientific contact and the friendly relationship among the electrochemists of the two countries. Since that time the Seminar was held regularly every two years in Moscow (2nd), Kyoto (3rd) and Kiev (4th) in cooperation of the Soviet and Japanese electrochemists. The problems discussed in the past seminar were focussed mainly on the basic ones in electrochemistry, particularly on the thermodynamical and molecular approaches to the electrode reactions and the electrified interphases.

In recent years in connection with the decrease of the world reserves of oil and natural gas, a severe economy has been imposed on the use of these natural resources, and the research and development of the large scale energetics have been induced explosively in many countries for the conversion of the solar radiation energy and the waste heat of atomic reactors. On the other hand, the recent advances in the study of electrochemical principles allow us to make a considerable contribution to the large scale energetics. This is the reason why the Japan Electrochemical Society and the Academy of Sciences of the USSR arrived at an agreement to discuss the fundamental aspects of the electrochemical energy conversion and electrocatalysis at the 5th JAPAN-USSR Seminar on Electrochemistry in Sapporo, Sept. 16-18, 1982.

Eight Soviet electrochemists, headed by Prof. V. E. Kazarinov, the Director of the Institute of Electrochemistry, Academy of Sciences of the USSR, and 50 Japanese electrochemists participated in this Seminar. The 5th Seminar was organized to include two

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sessions of oral presentation and round table discussion. Six Soviet and 4 Japanese papers reported at the Seminar were published in this Journal, vol. 30, No. 2 and No. 3, 1982, and other 23 papers will be published elsewhere. The present report concerns the proceedings of the Round Table Discussion at the 5th Seminar held with Prof. K. Honda, the University of Tokyo, and Prof. V. S. Bagotzky, the Institute of Electrochemistry, Moscow, in the chair on the subject "Perspective on the Electrochemical Energy Conversion in Future".

Prof. K. Honda (University of Tokyo):—

We really enjoyed the stimulated discussions at the 1st Part of the Round Table Discussion on the problems left to be discussed in the Oral Sessions. Now we are going to the 2nd Part of the Round Table Discussion which will be devoted to the perspective of the energy conversion through the electrochemical ways. We have several prearranged speakers from the Soviet and Japanese delegations who are ready to present topics on the perspective of the electrochemical energy conversion. We shall start from the presentation by Prof. Bagotzky on the place and role of electrochemistry in solving energy problem of the future.

Prof. V. S. Bagotzky (Institute of Electrochemistry, Moscow):—

In recent years the question of the possibility of using electrochemical devices in large-scale energy systems comes more and more often to the fore. The reason of this is: the search for new ways of solving energy problems arising in connection with the world energy crisis (approaching depletion of natural fuels) and the advances made in recent years in some areas of theoretical and applied electrochemistry. A comprehensive analysis of this question should take into consideration both the technological and the economical aspects of this problem. In addition, one should take into account the feasibility of solving a number of related electrochemical problems.

In the 60-ies in many countries extensive studies began on different systems of fuel cells, both for autonomous operation and for stationary plants. The results of these studies proved the possibility of designing satisfactorily operating fuel cells. Nevertheless at present fuel cells are not produced on a large scale and are not widely used.

The present situation with fuel cells seems to be caused by the fact that only three versions of such cells were brought to a high degree of perfection: alkaline hydrogen-oxygen and hydrazine-oxygen cells and hydrogen-oxygen cells with a solid polymer electrolyte. In nearly all versions platinum catalysts were used. In developing these versions insufficient account was taken of the specificity of various fields of their application. The main requirements for large-scale energetics are their adequate economic characteristics — the use not only of platinum catalysts but even of nickel-based electrodes is prohibitive from the point of view of costs. In the case of autonomous use of fuel cells the main requirement is convenience in operation. Evidently in most cases neither hydrogen stored in steel cylinders (or in bound form), nor toxic hydrazine com-

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plies with this requirement.

At present work on fuel cells for large scale power production from natural fuels proceeds in two directions: development of medium-temperature phosphoric acid cells for oxidation of hydrogen obtained by conversion of hydrocarbon fuel, and development of high-temperature cells with a carbonate melt for oxidation of coal gasification products. High temperature used facilitates solution of two important electrochemical problems: decrease of the hazard of poisoning the hydrogen electrodes with carbon monoxide and increase of the efficiency of the oxygen electrode.

Fuel cells of the first kind can find application for load-levelling. Their extensive use as base-load power stations is doubtful since by the moment they may become sufficiently developed (in approximately in 30-40 years) hydrocarbon fuel will lose its importance as an energy source. At the same time, the cells of the second kind hold much promise. Their possible efficiency is close to 50%, *i. e.* more than for other power plants.

The use of energy sources inconstant in time, such as wind and tidal power, solar energy, is impossible without intermediate energystorage. The most effective means of energy storage consists in converting it to chemical energy. Some attempts have been described at using conventional lead batteries. Such attempts, however, could be hardly described as promising, since a plant designed for storage of 100 MWh would require a battery with about 1000 tons of lead.

Development of efficient hydrogen-oxygen storage plants is hindered as yet by insufficient efficiency of the oxygen electrode. At the present level of development the overall efficiency of the plant will be rather low — about 50%. The problem of enhancing oxygen-involving reactions and decreasing polarization of the oxygen electrode is one of the central problems of electrocatalysis and entire electrochemistry.

Hydrogen is one of the promising energy carriers of the future and will find wide application both in energetics and technology. We are faced with the task of producing hydrogen not only at the expense of electrical energy but also by partial use of thermal energy of nuclear reactors. One of the ways to achieve this is high-temperature (at 800~1000°C) electrolysis of steam in electrolytic cells with zirconium dioxide based solid electrolyte. It is interesting to note that at high temperatures the oxygen electrode practically is not polarized and therefore such cells work well as reversible storage cells.

Another aspect of the problem of developing new energy carriers is synthesis of methanol-like substances by cathodic reduction of carbon dioxide. This is a comparatively new field in electrochemistry. The research being done now is of an exploratory character but from the view point of electrocatalysis it involves many interesting problems.

Different opinions are expressed in the literature on the prospects of using electrochemical methods for solving energy problems. The use of electrochemical processes

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has not only advantages in efficiency but also presents many difficulties. Some of these are fundamental (development of cheap and efficient catalysts for electrodes), the others are of a technological nature. It seems to me that the general development of applied and theoretical electrochemistry shows that these difficulties can be overcome.

Prof. Honda (University of Tokyo):—

We expect two reports from Japan side on thermochemical water splitting. First I would like to ask to Prof. Tamura to talk on the metal oxide electrodes for the electrolysis of water.

Prof. H. Tamura (Osaka Univ. Faculty of Engineering):—

We are studying the production of hydrogen by the electrolysis of water. As well recognized, the anodic process is rather difficult to proceed as compared with cathodic process, so our main interest has been focussed on the elucidation of the mechanism of the oxygen evolution reaction as well as the chlorine deposition on the dimensionally stable anodes (DSA) such as ruthenium and titanium electrodes. Apart from the mechanism of the anodic processes, my talk will be limited now to a modification of DSA by coating iron electrode surface with cobalt oxides. The surface of an iron plate is polished by emery paper or by etching in some acid and then put it into the solution of cobalt nitrate and then thermally decomposed at 450°C. The DSA prepared in this way is very cheap and has good activity and a long life; *i. e.*, the current density  $10^{-3}$  A/cm<sup>2</sup> at 0.63 V vs. mercury electrode after the operation of more than 1000 hours. The DSA of Ti covered with cobalt oxides is also proved to be of high activity as the modified iron electrode and its life is now under the test.

Prof. K. Honda:—

Now I would like to ask to Prof. Takehara to present the hybrid system of water splitting related to the oxidation of sulfur dioxide.

Prof. Z. Takehara (Kyoto University):—

I believe the development of technology for making effective use of nuclear heat and inexhaustible solar energy is important in near future. Heat and light from these energies cannot be easily stored and transported for a long distance by themselves. I would like to introduce our electrochemical research from a view point to construct the effective conversion devices of heat, light and electricity producing the useful energy carriers, *e. g.*, hydrogen and battery active materials, through electrochemical reactions. We can store the electric energy during the off-peak periods, *e. g.*, in the night, as hydrogen produced by water electrolysis. From the view point of lower energy electrolysis, *i. e.*, lower overpotential and ohmic drop, high temperature operation by using molten salts or solid electrolytes will be desired. By using porous cathode introducing water vapor in molten NaOH electrolyte or porous anode introducing water vapor in

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zirconia electrolyte, water can be electrolyzed with low energy. The development of stable and cheap electrode and cell materials will be the key technology.

Instead of the anode reaction of oxygen evolution, if we use the another anodic reaction, *e. g.*, the oxidation of  $\text{Fe}^{2+}$  ion to  $\text{Fe}^{3+}$  ion, we can get hydrogen at lower cell voltage. When the sulfuric acid solution containing  $\text{Fe}^{2+}$  ion is electrolyzed in the cell having a packed bed carbon anode and platinum cathode deposited on anion exchange membrane, we can get hydrogen and  $\text{Fe}^{3+}$  ion with less than 1.0 V at 50 mA/cm<sup>2</sup>. Such electrolysis can be progressed with less energy than that direct water electrolysis. However, produced  $\text{Fe}^{3+}$  ions have to get back to oxygen and  $\text{Fe}^{2+}$  ions. For such getting back process, we can use the solar light in the daytime. In the photo-electrochemical local cell having a n-type semiconductor anode illuminated with solar light, the electrolyte from electrolyzer was decomposed to oxygen and  $\text{Fe}^{2+}$  ions with quantum efficiency of about 10 times as high as that of direct water decomposition in the same cell. Now, we use rutile  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{WO}_3$  as the stable n-type semiconductors in sulfuric acid solution. However, in the case of  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$ , light of wavelength longer than 420 nm cannot be used effectively due to the bandgap of about 3.0 eV of these semiconductors. In the case of  $\text{WO}_3$ , the anode shows photo-sensitivity for light of shorter wavelength than 500 nm due to the narrower bandgap of about 2.7 eV. But, since the potential shift for the anodic reaction is small as compared to that of  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$ , the potential of  $\text{WO}_3$  anode must be shifted to cathodic side about 0.45 V by connecting the silicon solar cell in series, in order to work effectively as anode of photo-local cell. Under present condition, we cannot use effectively the light of wavelength longer than 500 nm, which is the major constituent in solar light. We must investigate to find the suitable semiconductor. Secondary, for such getting back process, we can use the thermal energy from sunshine or nuclear fission of less than 1000°C effectively. We can get more concentrated sulfuric acid solution containing  $\text{Fe}^{2+}$  ions from the produced electrolyte containing  $\text{Fe}^{3+}$  ions in electrolyzer by the rapid reaction with  $\text{SO}_2$  gas in the packed tower, with carbon catalyzer. By repeating electrolysis and reaction with  $\text{SO}_2$ , we can produce the enriched sulfuric acid solution containing  $\text{Fe}^{2+}$  ions, *e. g.* 5 M  $\text{H}_2\text{SO}_4$  with 0.3 M  $\text{FeSO}_4$ . By vaporizing water, we can get easily 10 M  $\text{H}_2\text{SO}_4$  after separation of  $\text{FeSO}_4$  precipitate. By introducing 10 M  $\text{H}_2\text{SO}_4$  on the quartz glass particles at 400°C and then by introducing produced gas mixture of  $\text{SO}_3$  and  $\text{H}_2\text{O}$  on the  $\text{Fe}_2\text{O}_3$  catalyzer deposited on  $\text{Al}_2\text{O}_3$  powder, we can get oxygen and  $\text{SO}_2$  which is recycled to the packed tower. Now, we have constructed the bench-scale plant for hydrogen production of about 10 l hr<sup>-1</sup> of 25°C, 1 atm by such hybrid process combined with assistance of thermal energy about 27 kcal hr<sup>-1</sup> of 400°C and 27 kcal hr<sup>-1</sup> of 800°C and electric energy of about 20 W (5 V, 4 A).

We can also store the electric energy by charging the batteries in the load leveling systems. High temperature batteries can give us higher energy conversion efficiency

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than conventional low temperature batteries. From the viewpoint of high energy conversion, we are investigating Li alloy-Cl<sub>2</sub> battery with molten electrolyte of KCl and LiCl and Na-O<sub>2</sub> battery with  $\beta$ -Al<sub>2</sub>O<sub>3</sub> and molten NaOH electrolyte. Then, we can save energy by using fuel cell type reactor, where production of chemicals proceeds with a simultaneous recovery of electric power. So, we are investigating H<sub>2</sub>-Cl<sub>2</sub> cell with molten electrolyte of KCl and LiCl and CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>-Cl<sub>2</sub> cell with molten electrolyte of KCl and LiCl containing Cu<sup>2+</sup>/Cu<sup>+</sup> couple, in order to recover simultaneously the electric power from a chlorination process of hydrogen and hydrocarbons. I think the caustic soda and chlorine production by the use of oxygen cathode is one of the process in such viewpoint. Although we cannot get hydrogen, we can save the electric energy corresponding to H<sub>2</sub>-O<sub>2</sub> fuel cell. I believe that the electrochemical process has an important role in the fields of the effective production of storable chemical energy and the energy saving, and that the developments of the process relating to new or future energy systems and the heat and corrosion-resisting new materials with high performance in severe environments are important.

Prof. V. S. Bagotzky:—

Next report will be ready by Soviet delegation Prof. Gorodysky on the aspects of solid electrolytes.

Prof. A. V. Gorodysky (Institute of General and Inorganic Chemistry, Kiev):—

I would like to discuss one special question which plays a certain role in electrochemical energy conversion systems. I think that in such systems we have now two problems to be solved. The first problem concerns electrocatalytic electrode materials and the second solid superionic electrolytes. We have paid rather great attention to electrocatalytic processes. But we have not discussed so much about the question of superionic electrolytes.

In this connection I would like to attract your attention to our understanding of the phenomenon of superionic conductivity.

When we have a system of metallic lithium and molten lithium chloride it could be one of the best systems for storage cells. But metallic lithium is dissolved unlimitedly in molten lithium chloride. We must employ a diaphragm of solid electrolyte which purpose is to prevent lithium dissolution into the electrolyte. This diaphragm must not be only solid but it can be a liquid substance. The only requirement for this diaphragm is to prevent chemical solution of metal into the electrolyte and not to prevent ionic current passage. To improve the synthesis of superionic conductors we must understand how these properties change for a variety of substances. When we have a system of metallic zinc in water we see that in spite of the thermodynamic properties the metal does not dissolve in water. There is a special layer which prevents such dissolution. It is obvious that this layer is a superionic conductor. Thus we can in a certain degree

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unite the phenomenon of passivity and that of superionic conductivity.

Now, we usually assume that a superionic conductor has to have only ionic conductivity but not electronic conductivity. Let us consider zinc electrodeposition from an aqueous solution. One usually means that such electrodeposition is possible due to high hydrogen overvoltage on the zinc surface. But there are many systems in which intermediate phases on the electrode surface appear. These films are mixture of zinc oxide and zinc hydroxide. These films have a mixed conductivity, electronic and ionic. From the metallic side the film, due to its ionic conductivity, is reduced to metal. From the electrolyte side this film, due to its electronic conductivity, works as an electrode and regenerate itself. This film is a diaphragm which separates the electrode and the electrolyte. And naturally we can also consider this film as a superionic conductor which prevents the penetration of atomic forms of metal into the electrolyte and prevents ionic current exchange between the electrode and the electrolyte. Thus such superionic conductors include a rather big class of substances with rather different properties. The study of these substances is very useful for a variety of electrochemical problems.

Prof. V. S. Bagotzky:—

Next Soviet delegation Dr. Radyushkina, with the topic perspective on the use of organic complexes in electrocatalysis.

Dr. K. A. Radyushkina (Institute of Electrochemistry, Moscow):—

Up to 1975 electrocatalytic studies were mainly connected with platinum like metals. During the last ten years the number of electrocatalytic systems was significantly extended including binary metallic alloys and non-metallic catalysts. At present a research for new electrocatalysts on the basis of non-metallic systems without noble metals appears to be the most prospective direction. Non-metallic catalysts include carbon containing materials, oxides, organic complexes of metals and high molecular compounds on its basis as well as biocatalysts that is enzyme systems.

Advantages and merits of non-metallic catalysts can be shown by considering as examples two important reactions, namely oxygen electroreduction and sulfur dioxide electrooxidation. The reaction of oxygen electroreduction at metallic electrodes was intensively studied by electrochemists of many countries. By the present time the reaction path has been established and the kinetic regularities of individual steps have been determined for these multistep processes at various electrode materials.

However, in spite of the large efforts which have been made in the study of this reaction at metallic electrodes the problem of developing a reversible oxygen electrode has not been solved.

As it is known, the reversible oxygen potential has been realized. But it was achieved by inhibition of all side processes resulting in deviation from the equilibrium, but not by acceleration of the oxygen reaction itself.

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Organic complexes of some metals seem to be more prospective for activation of oxygen electroreduction to reach the reversibility region of the oxygen electrode reaction. These complexes contain ions of cobalt, manganese or iron in the molecule centre and coordinate of the oxygen molecules very well. One some organic complexes, for example, phthalocyanines of iron and porphyrin of cobalt, the oxygen electroreduction to water involve breaking of the O-O bond.

Use of metalloporphyrins as promoters of carbon-containing materials led to development of active and stable oxygen electrode for acid media. The same mechanism with the first electron transfer as rate-determining step is retained for metalloporphyrins in acid media.

Complexes of metal, in particular metalloporphyrins, are models of the active center of some natural biocatalysts or enzymes. Enzymes are of interest for electrocatalysts owing to high reaction rates in their presence as well as their selectivity. The fact is also of importance that according to the published experimental data enzymes retain their molecular structure and characteristic enzymatical properties in the immobilized state.

In the presence of immobilized laccase on carbon-containing materials a potential equal to 1.21 V (NHE) close to reversible oxygen potential was established. There are well known difficulties at investigation and application of enzymes connected with electrodes. Therefore it is prospective to use simple organic complexes of the metals that is oxidase models instead of real enzymes.

The second reaction is anodic oxidation of sulfur dioxide. Interest in this reaction is connected with its use in the combined thermoelectrochemical cycle of hydrogen production from water at the expense of nuclear reactor heat. Platinum and its alloys with gold are active catalysts for this reaction. Organic complexes of cobalt have high activity in this reaction (close or higher than the activity of platinum). But these catalysts have a very important advantage over platinum, namely they are not deactivated by sulfur-containing particles.

Prof. S. Toshima (Tohoku University):—

We are studying the CO<sub>2</sub>-reduction by porphyrin, but its life time is very short. Can you tell me how to make the life time of the electrode to be longer?

Prof. Radyushkina:—

Such type of catalysts as phthalocyanine is indeed not stable but after the heat treatment of the catalyst at 600~800°C the catalyst is already very active and very stable, its life time is more than one year and now no problem to use such type of materials.

Prof. K. Honda:—

I would like to ask to Prof. T. Osa a talk with very interesting title of two hundred

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percent current efficiency in electrolysis.

Prof. T. Osa (Tohoku University):—

I would like to propose a new idea of 200% efficient electrolysis using electrocatalytic reaction.

Prior to this proposal, I show you some metal porphyrins synthesized in my group. The structure of water-soluble tetrakis(N-methyl-4-pyridyl) porphyrinatoiron [Fe(III)TMPyP] is shown in Fig. 1.

This iron porphyrin is active to electrocatalytic reduction of oxygen as discussed later. Other porphyrins possessing phyrophilic substituents on aromatic rings, some of them are water-soluble and also active to oxygen reduction :

tetrakis (*p*-carboxyphenyl)porphyrin  
 mono-*p*-carboxyphenyl-triphenylporphyrin  
 tetrakis(*p*-hydroxyethylphenyl)porphyrin  
 tetrakis(*p*-aminophenyl)porphyrin  
 tetrakis(*o*-aminophenyl)porphyrin  
 mono-*p*-aminophenyl-triphenylporphyrin  
 mono-*o*-aminophenyl-triphenylporphyrin  
 central metal ion: Fe, Co

These porphyrins can be attached covalently on electrodes using the substituents like Fig. 2.

The electrocatalytic activity of Fe(II)TMPyP for oxygen reduction is demonstrated in Fig. 3. **A** is a cyclic voltammogram of  $2 \times 10^{-4}$  M Fe(III)TPyP, **B** is that of air-saturated oxygen itself, and **C** is that of mixture of  $2 \times 10^{-4}$  M porphyrin and air-saturated oxygen. All the voltammograms were measured in aq. 0.05 M H<sub>2</sub>SO<sub>4</sub>.

As seen here, the reduction current increased like **C** at the same reduction potential of Fe(III)TPyP (ca. -50 mV vs. SCE). These results together with some other electrochemical measurements suggest the following mechanism :

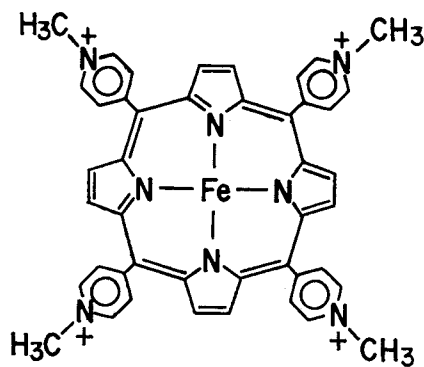
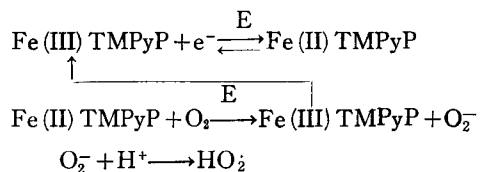


Fig. 1. The structure of tetrakis (N-methyl-4-pyridyl) porphyrinatoiron [Fe(III)TMPyP].

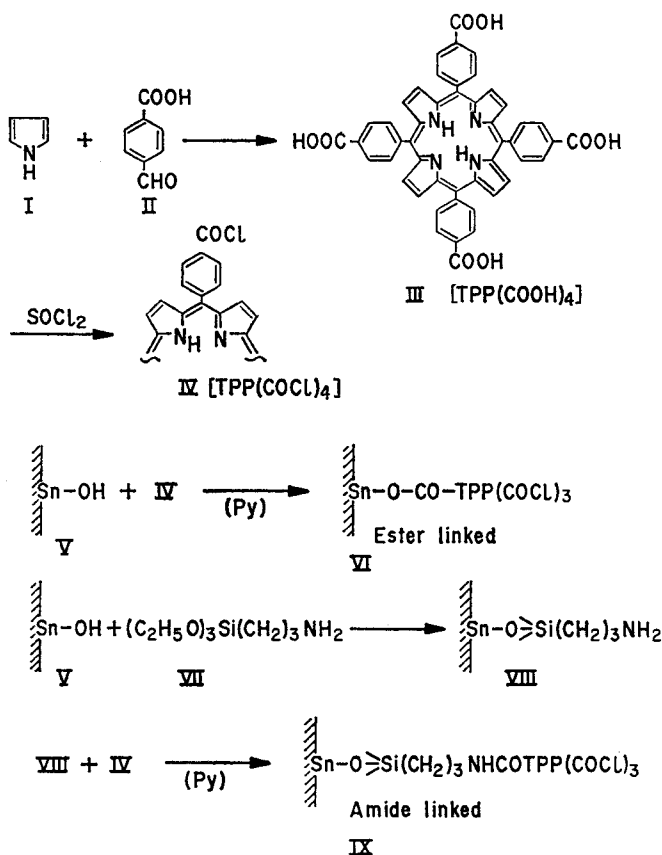
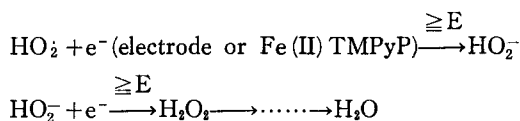
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Fig 2. The modification of the electrode surface by TPP(COCl)<sub>4</sub> with ester and amide linkages.



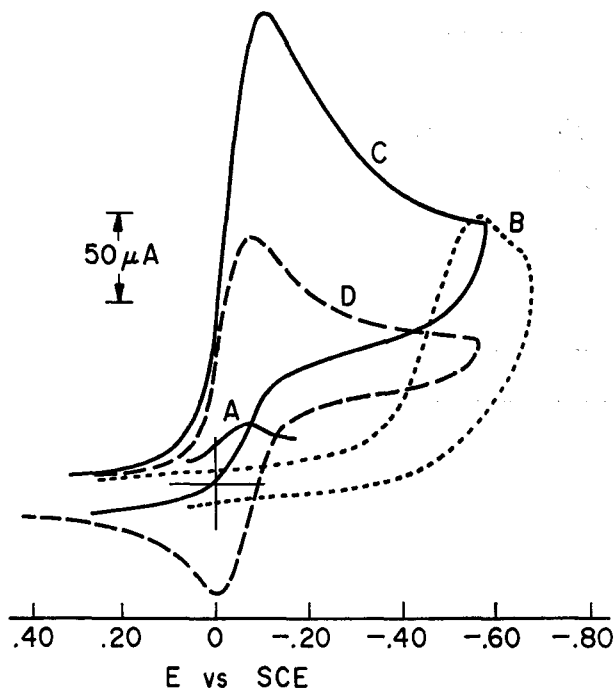
Therefore, oxygen is electrocatalytically reduced at a positive cathodic potential to hydrogen peroxide and sometimes to water.

Now, I show you 200% efficiency of electrolysis. At the cathode, if the foregoing reactions are carried out, hydrogen peroxide and/or active intermediate species of oxygen can be used for oxidation of organic compounds. For instance, toluene is oxidized to benzaldehyde and cresol mixtures (Fig. 4).



This kind of reaction proceeds more than 100% current efficiency due to autoxida-

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**Fig. 3.** Cyclic voltammograms at Tokai glassy carbon electrode. **A:**  $2 \times 10^{-4}$  M Fe(III) TMPyP, **B:** only  $O_2$  (air-saturated), **C:** mixture of  $2 \times 10^{-4}$  M Fe(III) TMPyP and  $O_2$  (air-saturated), and **D:**  $10^{-8}$  M Fe(III) TMPyP, no  $O_2$ . All solutions contain 0.1 N  $H_2SO_4$ . Scan rate: 0.11 V/sec.

tion mechanism in the presence of oxygen. The anode can also be used for electrochemical oxidation.

Therefore, it is concluded totally that 200% efficient electrolysis can be achieved using electrocatalytic reduction of oxygen.

Prof. Bagotzky:—

What is the reaction at anode?

Prof. Osa:—

I did not mention it in details. The activation of oxygen at anode is not usually easy, although some reports have described the mechanism forming active oxygen.

Prof. Bagotzky:—

Oxidation of organic compounds?

Prof. Osa:—

Yes.

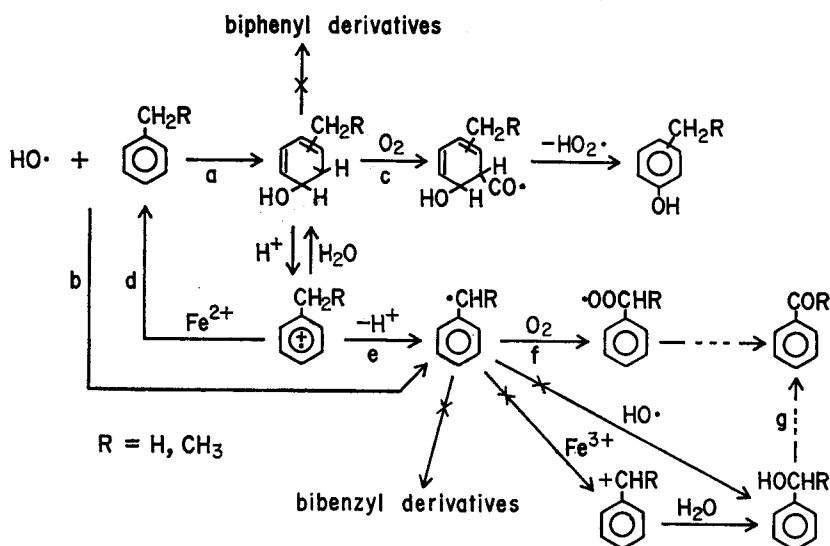
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Fig. 4. Schematic mechanism for oxidation of toluene and ethylbenzene by electrogenerated hydroxyl radical.

Prof. Bagotzky:—

Epoxidation?

Prof. Osa:—

Precisely speaking, oxygenated compounds, usually non-epoxy compounds, are formed at the anode. In the case of toluene, it is also oxidized to benzaldehyde and benzoic acid on Pb anode in acidic (H<sub>2</sub>SO<sub>4</sub>) solution.

Prof. Radyushkina (translated by Prof. Bagotzky):—

I would like to comment to the mechanism of oxygenation. It is said that such a correlation between catalytic activity of metal complex and redox potential was often used in literatures but it is not quite distinct correlation between these quantities. Oxygenation seems not to proceed directly but rather proceed through some kind of coordination of oxygen molecule to metal complex, charge transfer to organic substances and so on. Therefore, it shows very complicated dependence upon the nature of the centered metal ion used. This is our point of view.

Prof. Osa:—

Your comment is very reasonable considering the detailed mechanism of metal porphyrins with oxygen and organic substances.

Prof. B. S. Bagotzky:—

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Further discussion by prof. Pshenichnikov with topics related to the idea about the electrochemical method of energy conversion.

Prof. A. G. Pshenichnikov (Institute of Electrochemistry, Moscow):—

We can consider two directions of applicability of electrochemical method in energetic systems. The first direction is the creation of electrochemical systems in which the main aim of research is to produce or storage electrical energy. In that connection I would like to point out that in our session a number of communications have been presented about very interesting systems which may be called intercalation systems. There are many examples of such system, *e. g.* hydrogen/metal alloy systems, lithium/oxide or sulphide systems, polymeric films a. o.

The second very important direction of application of electrochemical methods in energetics problem is the production of active energy carriers. The most promising agent of such type is considered hydrogen, and large scale electrolytic hydrogen production is very important art for future power systems.

On that method we have presented two reports in which results with alkaline and solid polymer electrolytes have been shown. It seems to be possible to obtain a current density of about  $1 \text{ A/cm}^2$  with the voltage about  $1.6 \sim 1.7 \text{ V}$  and at  $2 \text{ A/cm}^2$  about  $1.5 \text{ V}$  which is so called thermo-natural voltage. That is a very interesting point of scale up of electrochemical application in future energy production.

Prof. K. Honda:—

Next speaker, Dr. Fujishima, with topics on semiconductor electrode on energy conversion.

Prof. A. Fujishima (University of Tokyo):—

Now many electrochemists are studying semiconductor electrode reactions in order to convert solar energy to chemical or electrical energy. Fig. 5 shows an example of photoelectrochemical cell (PEC) just a semiconductor  $\text{TiO}_2$  immersed into the solution and connected to a metal electrode.

With using this PEC the possibility of solar photoelectrolysis of water was demonstrated by us for the first time.

For the construction of an efficient

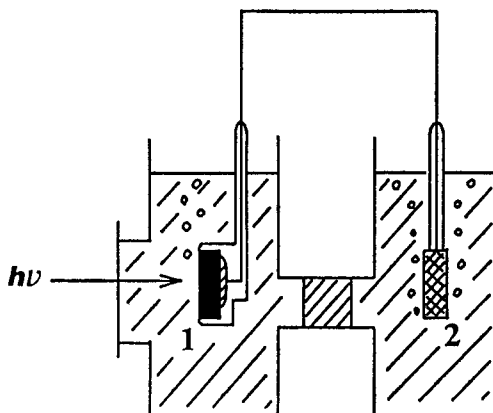


Fig. 5. A photoelectrolytic cell in which a  $\text{TiO}_2$  electrode (1) is connected with a platinum electrode (2).

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PEC with which water is decomposed to  $H_2$  and  $O_2$ , the following conditions are required for n-type semiconductor photoanodes: long-term stability during photoelectrolysis; negative flatband potential; smaller bandgap; and high quantum efficiency.

A large number of simple and mixed oxides have been examined by many researchers for the photoeffect and possible utilization as electrodes for water splitting under solar irradiation. However, as for only large-bandgap oxides have been found to be stable against photocorrosion with reasonable photoelectrochemical characteristics.

To improve the efficiency of water photolysis in a PEC, it is desirable to use smaller bandgap semiconductors such as Si and GaAs. However, these non-oxide semiconductors are unstable in electrolyte solutions resulting easily in surface dissolution or formation of an insulating oxide film. In view of this, coatings of these unstable semiconductors with a film of stable metals or semiconductors, or addition of a common redox couple have been attempted.

In the latter case, as the redox couple is reacting at both the photoanode and the metal cathode, there occurs no net chemical energy storage but electrical energy can be withdrawn in the external circuit. This type of PEC is called a regenerative photovoltaic cell, and about 13% has been obtained as the maximum solar energy conversion efficiency.

For a practical application of PEC, inexpensive methods for the preparation of large area semiconductor electrodes must be sought. Thus far, the following methods have been proposed: electrochemical oxidation or codeposition technique, chemical vapor deposition (CVD) technique, thermal formation technique, sintering of semiconductor powders, and vacuum evaporation technique.

Prof. V. S. Bagotzky:—

What is your opinion about the possibility of commercial application of the photoelectrochemical devices?

Prof. A. Fujishima:—

I think it may be possible to convert the solar energy to electricity and/or chemical energy, with the photoelectrochemical processes, because the solar energy conversion efficiencies have increased up to 13~14%, so far.

Prof. K. Honda:—

I would like to ask to Prof. Toshima to present your opinion on the future of electrochemical energy conversion or may be your philosophy on it.

Prof. S. Toshima (Tohoku University):—

It is quite difficult to answer exactly for the comments by Prof. Honda. Up to the present, we have been studying three themes about applied electrochemistry. The first one is high temperature fuel cell employing carbonate melt, so called 2nd generation

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fuel cell, and the second one is mixed valency metal complexes display devices, an electrochromic display using prussian blue which is a kind of pigment. The third one is electrogenerated chemiluminescence (EGCL). This is most charming subject in relation to an energy conversion from electrochemistry to light directly. We gave up the research of EGCL about 5 years ago, though we had carried out many works during about 10 years. The main reason was based on the decay of the electrode characteristics, originating from contamination by polymers or impurities formed on the electrode.

The electrochromic display device is the most interesting. As is well known, liquid crystal serves as an excellent display device, but its function is completely physical. In contrast, an electrochromic display is completely electrochemical and has many advantages in terms of efficiency, colour, contrast and memories. We are dealing with prussian blue and tungsten oxide, an electromotive force of  $WO_3$  system was presented and discussed in this seminar. We can expect other multicolour system which will compete with host guest liquid crystal system in near future.

The carbonate molten salt fuel cell is a promising electric producing plant to be prevailed in the second generation. There exist many difficulties concerning electrodes, electrolytes, constitution materials and housing. We are now investigating on those matters in the researches of the reduction of oxygen and the oxidation of hydrogen, carbon monoxide and methane. This fuel cell system will be developed to a local electric plant for domestic utility in 21st century.

Prof. K. Honda :—

**Conclusive Remarks**

The present discussion session is planned in view of the extreme importance of the energy problem. I would like to thank to all participants, particularly the speakers of topics for the really interesting and extremely informative discussions. Among a variety of the energy conversion pathways, it is quite sure that the electrochemical energy conversion plays the most important role.

The usual type of the electrochemical energy conversion is of course indispensable. In addition to that, the interesting new systems and ideas are presented. The scale up of the fuel cell performance, electrochemically formed hydrogen as energy carrier, superionic conductor, bioelectrocatalysis, electrochemical fixation of  $CO_2$  photoelectrochemical conversion etc. all seem to be suggestive.

We are convinced that the electrochemistry will constitute the essential basis of any kinds of energy conversion and contribute to solve the energy problem in the future.

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