TRENDS IN ELECTROCHEMISTRY

Edited by
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Foreword

This volume presents plenary lectures and invited papers that were delivered during the Fourth Australian Conference on Electrochemistry held at The Flinders University of South Australia, 16-20th February 1976.

Electrochemistry for a Future Society was selected as the Conference theme since the organising committee were mindful of the rapid change in technological perspective which the world now faces. We no longer have a prospect of uncontrolled spontaneous expansion and change as the result of technological enterprise. Rather, we face the task of attempting to reach a state of very restricted growth. In the next few decades special accent must be placed on minimizing pollution and maximizing the efficient utilization of all available energy sources.

With this in mind, the Conference organisers considered that a conventional electrochemistry symposium, with its divisions into the various academic aspects, would be less relevant than a meeting devoted to aspects of electrochemistry which may underlie parts of the new and necessary technology for the future state of affairs. What has actually been achieved by the Conference organisers is a balance between the ideals expressed and the resulting response from electrochemists. This response has a bias which reflects the dominance of certain resources, e.g. metallic minerals, within Australia. Consequently, the papers included in *Trends in Electrochemistry* cover subjects which are of both global and local concern.

EDITORS	J.O'M. BOCKRIS
Melbourne	D.A.J. RAND
June 1976	B.J. WELCH

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ELECTROCHEMISTRY FOR A FUTURE SOCIETY

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PART 1 DIFFICULTIES OF THE PRESENT SOCIETY

Indigestion: The Pollutional Danger

Pollutional difficulties arise from the automobile and from factories. Effluents from the latter can be dealt with, and have been in Japan and England. Effluents from cars are dealt with well in laboratories but the introduction of catalytic converters into cars lessens their performance and the catalytic purification is expensive and short-lived. Removal of lead from petrol increases pollution from unsaturates. If growth of the economies continues, the pollution rate will increase again in the 1990's (Fig. 1).*

Starvation: The Exhaustion of the Fossil Fuels before the Abundant Clean Energy Sources have been Engineered

Estimation of the time of exhaustion of the present fuels is not difficult to make if a given growth rate of the economy is assumed. A cessation of growth in our economy brings depression; growth in energy demand is, in any case, difficult to stop, particularly as the population of most areas of the world is still growing. If we assume a continuance of a 5% growth rate in energy need (the U.S. one has been 5.8% for some years), there will be exhaustion** of world oil by 1995. However, this assumes continued

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* This figure was given to the author by Dr. C. Heath, then of Esso Research, Engineering, Linden, N.J.

** "Exhaustion" is taken arbitrarily as the situation where scarcity has forced a (real) price rise 4 times that of 1976 (i.e. ten times that of 1973).

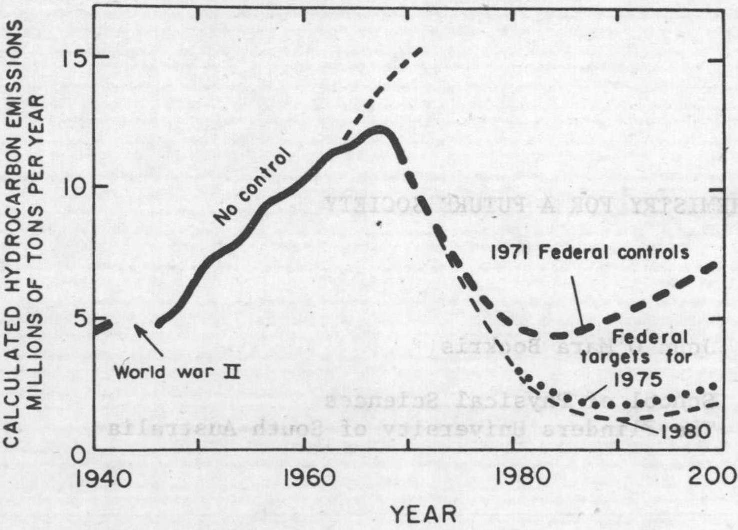

Fig. 1 Estimated effect of federal controls in the U.S.A. on hydrocarbon emissions from passenger vehicles. A rising trend is expected after 1985 because of the increasing numbers of cars.

export of oil from the Middle East. Saudi Arabia, the main supplier, plans to cease exports in 1990 and divert the rest of its resources to a planned indigenous industry (1).

After the exhaustion of gasoline and natural gas, synthetic fuels from coal are planned to bridge the gap until atomic and solar sources have been researched, developed and built.

Gross over-estimates of the supply of coal have been published (2); they omit the effect of growth and the fact that the coal production extrapolation line (from which is calculated the exhaustion date) is based upon the use of coal largely for electricity production (15% of need). When coal products take over from oil the use-rate would increase many-fold. Turner and Elliot (3) have allowed for this in Fig. 2, (see also Table 1 taken from Linden (4)).

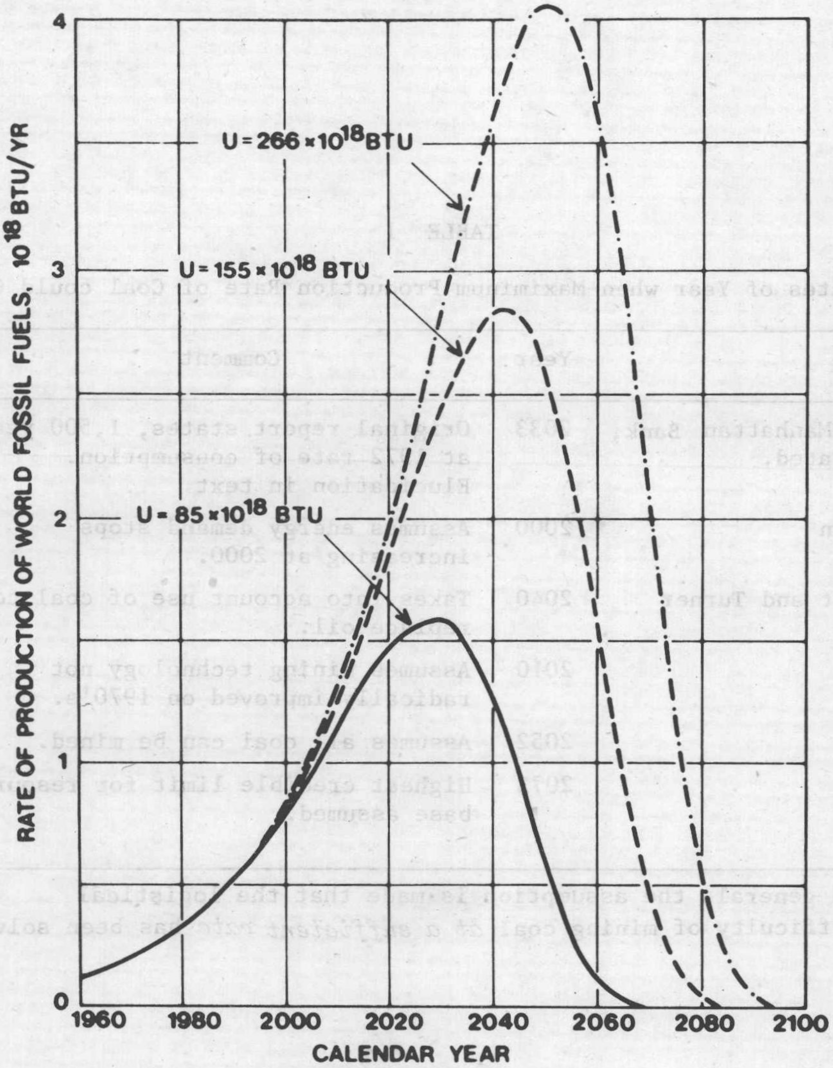

Fig. 2 Effect of the resource base on the projected rate of world fossil fuel yields. (Turner and Elliot (3)).

TABLE 1

Estimates of Year when Maximinum Production Rate of Coal could Occur*

Source	Year	Comment
Chase Manhattan Bank, elucidated.	2033	Original report states, 1,500 years at 1972 rate of consumption. Elucidation in text.
Brennan	2000	Assumes energy demand stops increasing at 2000.
Elliott and Turner	2040	Takes into account use of coal to replace oil.
Linden	2010	Assumes mining technology not radically improved on 1970's.
Linden	2052	Assumes all coal can be mined.
Linden	2073	Highest credible limit for resource base assumed.

* In general, the assumption is made that the logistical difficulty of mining coal *at a sufficient rate* has been solved (4).

A Latter-Day Coal Age?

The use of coal to replace oil on a large-scale seems improbable for the following reasons:-

1. There are difficulties of extracting coal at the rate needed. These have been stressed by Arthur (5). *Five* new mines of average size per day in the U.S. would have to be completed between now and 2000.

2. The pollutional problems which would be provided by the use of dirty American coal (much of it 5% sulphur) are great. Although it may be feasible to reduce the sulphur in coal in laboratory experiments, the economics of doing this on a large scale (massive milling to small particle size) and the degree of removal create difficulties. Were the rate of burning of coal increased not only seven times - needed to replace oil - but three times more to allow for energy growth to 2000, a disagreeable increase in air pollution seems probable.

3. Amortisation: a massive development of the coal industry is unlikely because it would need a guarantee of continuity of use through 30-40 years. This will not be possible except by Government Fiat.

A population of 10^{10} people would need 2000 reactors, each 40,000 MW. The population of the United States would need 40 large reactors, built in about 40 years to have an all breeder atomic energy economy by 2016. This is not an impossible amount of investment capital per year, but the breeder technology - after 20 years research - is not yet ready and the pollutional problems of the wastes are regarded by some as insoluble.

Conservation

Although some contraction in energy spending per person can be achieved by caution, a decrease of energy per person of $> 10\%$ would lead to deprivation (6) and hence political unrest. The population of most countries continues to grow inexorably. A cutback in energy demand, or even stopping of growth, is an impractical expection with democratic (i.e. low control-power) governments. That political party will be elected which makes most credible its promise of the highest standard of life in the *immediate* future.

Democracy must therefore drive an economy at full speed to exhaustion of its resources. Of course, whilst the capital lasts, the standard of life in the "spend what we have" democratic society will be greater than that in the Economy which holds off consumer spending so as to obtain an industrial base to build military forces and energy production, i.e. Long Term Strength.

Media Of Energy

Fossil fuels are sources and media of energy. However, the *new* sources will give electricity or heat at source.

Heat is not a suitable medium of energy because it cannot be transported. One possible medium is electricity, but it is not suitable for long distance transport of energy nor for carrying out tasks now carried out by natural gas.

Thus, were we to use electricity, even though there were no difficulties in respect to the cost of sending it over large distances (as needed with solar sources), one would have to research and develop electrochemical technology. Such technology is only at the point of projection from the fundamental stage.

There is need for a fuel easily produced by heat or electricity and easily transportable. Hydrogen is likely to be useful. It could interface with electrochemical devices, viz. fuel cells. The alternative is methanol. Internal combustion devices driven off methanol at 30% efficiency would have to compete with the fuel cell driven cars which function off hydrogen at 60% efficiency.

Electrochemical Consequences

One consequence of the new energy sources is a rebuilding of much technology toward utilising electricity, hydrogen and methanol. At source, the cost of these fuels will be electricity $<$ hydrogen $<$ methanol; hydrogen will always be cheaper than the product of the reaction with CO_2, methanol. A greatly increased component of electrochemical technology therefore arises on economic (and of course, ecological) grounds.

PART II ELECTROCHEMISTRY

Definitions of Electrochemistry

There are misunderstandings of what electrochemistry is. It was originally discussed in terms of electrode process-chemistry as exemplified by Faraday and Nernst. The European concept of electrochemistry ended with Tafel (1903) and the birth of electrode kinetics.

In this early era, there was less concentration upon ionics. This was awakened by Arrhenius. The parallel development of the electrode and ionic theme within electrochemistry was thus begun.

The Nernstian hiatus occurred between 1900 and 1950. Ionics prospered because of the application of statistical mechanics to the properties of solutions and a fruitful approximation which made ionic systems the centre of physico-chemical discussions from about 1925 to 1945. Ionics became asymptotic by the 1960's and by 1970 most of the remaining fundamental interest went into the study of the ionic environment.

The 1950's saw the rebirth of the electrode process interests, sparked by vigorous British and German schools. An International Society for Electrochemistry was formed. The phenomenological theory of electrode kinetics became established (7).

During the 1960's the terms Ionics and Electrodics (8) were coined. It was a time of excitement in electrochemistry for the field played a part in space technology and was seen by some* to offer an interesting alternative technology. This brilliant phase saw the birth of the concept of Electrochemical Science (9): electrochemistry is no longer a part of Chemistry but stands as an interdisciplinary subject, see Table II.

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* For a few years in the mid 60's, electrochemistry was a subject of interest in Washington Government circles. Fuel cells and electrochemical developments became something of a political football because of the considerable effects on the automotive industry. Thus, the field and its leading exponents, world-wide, was subject to study by the American Security Services.

TABLE II

Electrochemistry, a Perspective from Afar

Period of Early Discovery	Nernstian Hiatus	Rise of Ionics	Electrochemistry Becomes Predominantly Concerned with Interfaces	Electrochemistry Becomes an Interdisciplinary Area
Muscles move when currents pass.	Over-thermodynamical approach prevents development of charge transfer kinetics at interfaces.	Study of ions in solutions, adjunct to electrochemical studies, becomes identified with electrochemistry itself in England and America.	The kinetics of electrical reactions at interfaces is formulated, and some basic progress in investigating its mechanisms is made.	Electrochemistry plays a role in space power, stability of materials, functioning of biological cells, nylon synthesis, vehicular transportation.
1791	1910-1940	1920-1940	1950's	1960's

Relevant Aspects of Electrochemistry

1. Many problems of syntheses, materials science, engineering and biology are associated with electrochemistry. Interfacial properties are electrochemical in the sense that all interfaces are charged, and the situation at them is electrochemical.

2. Electrochemical reactions can go up and down the free energy gradient, depending on the interfacial monolayer charge.

3. The range of fields in science in which the important step is electrochemical is comparatively great. Examples of the interdisciplinary character of electrochemistry have been given in a well-known book (10). Concepts of electrode processes underlie much Analytical Chemistry. In Metallurgy, stability is based upon electrochemical kinetics. In Engineering, much energy production and storage is electrochemical in prospect. In Biology, the applications of electrochemistry are legion, the most well-known one being the transmission of electric currents in nerves, and the most recent, the influence of potential on the growth of bones.

4. Electrochemistry is "another chemistry"? There seem to be usually two ways of doing things - the normal thermochemical way or by an electrochemical alternative. The Van't Hoff Law relates cell potential and free energy. Many reactions, for example Kroll's synthesis of Ti, can be looked at in terms of collisons of particles and solutions, but such reactions may be considered alternatively in terms of interfacial reactions. Cracks in metals and their spread can be viewed in terms of mechanics and stress, but there is an electrochemical aspect in the anodic dissolution at the tip of the crack. Are biological reactions collisonal reactions in solutions, or are they interfacial reactions occurring through charge transfer at interfaces?

5. In future towns, energy will come from atomic and solar sources; the medium for the energy will be electricity or hydrogen; the town is likely to be self-contained (materials recycled) except for its energy supply. At first CO_2 will be rejected into the atmosphere but if energy costs can be sufficiently reduced, it may be advantageous to recycle the CO_2. The processes which run the recycling must be non-polluting and many are therefore likely to be electrochemical. Transportation is likely to use stored electricity or hydrogen-working fuel cells (the only alternative is methanol); many machining processes and recovery of materials seem likely to be electrochemical. Polluted liquids will be electrodically regenerated.