

# THEORY OF POROUS ELECTRODE OPERATIONS

S. K. RANGARAJAN

*Homi Bhabha Fellow, National Aeronautical Laboratory, Bangalore-17*

**1. ELECTROCHEMICAL** energy conversion devices (and especially those with high-energy density applications) employ porous electrodes extensively. Be it a primary battery like silver-zinc or a storage device as lead-acid (or nickel-cadmium) or certain important fuel cells, electrodes with a high specific surface as offered by porous media are needed. This is essentially because the electrode current attainable under given conditions is not only a function of the potential but is also dependent on the extent of the surface available for the electrochemical reactions to take place. Since in many cases the reactions that are otherwise desirable may be very slow to proceed, the rate of the reaction is more conveniently enhanced to the required extent by an increase in the area factor. And so the porous electrodes that are able to provide a large active surface area become well-nigh indispensable. But this same factor, *viz.*, an effective pore wall surface, introduces difficulties in the operations in the form of limitations due to associated phenomena like mass transfer, charge transport, etc. It is as if some of the advantages are lost on the way. A theoretical formulation of such real system operations is obviously a formidable task. We discuss below types of simplifications introduced in the models—their nature and their motivation.

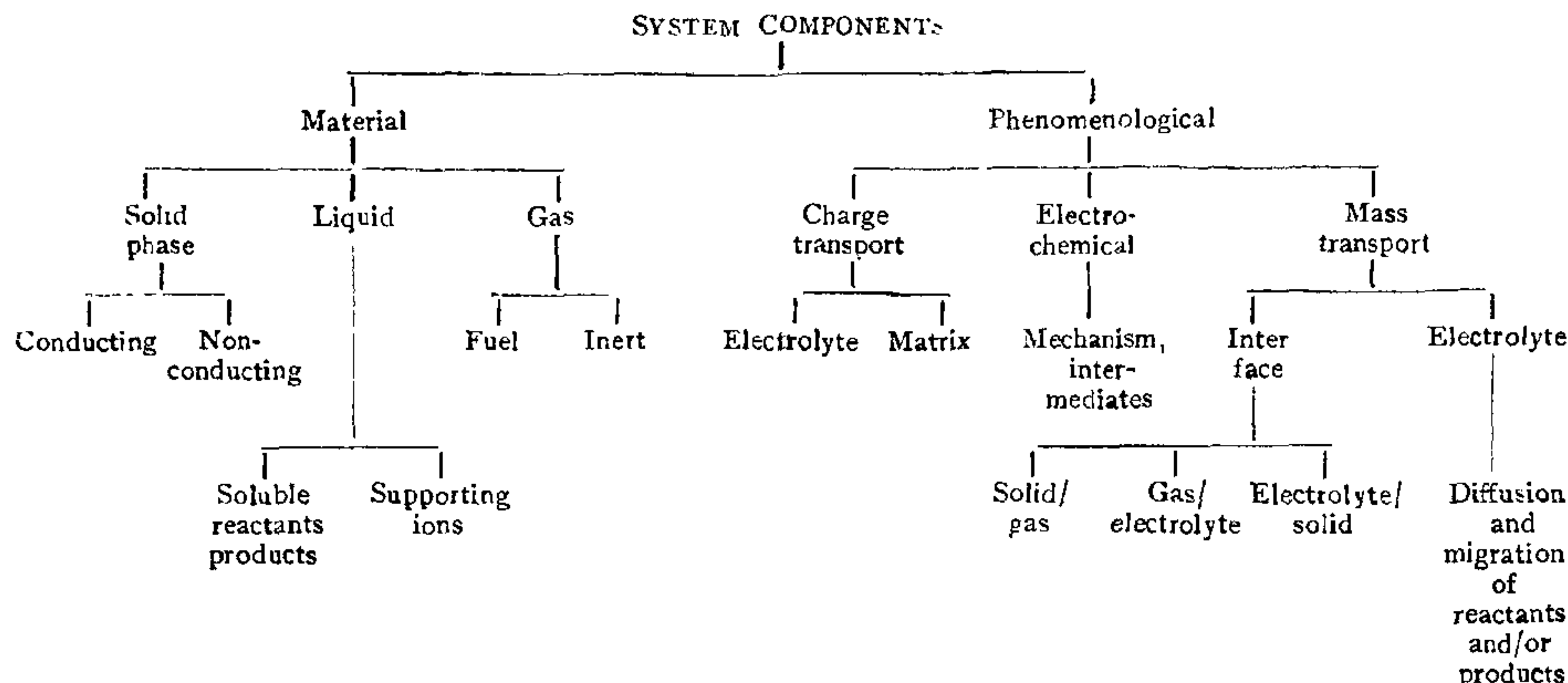
A porous body can be viewed as a medium wherein particles (or voids) are distributed in a random or ordered fashion. The many parameters defined to characterise real porous systems—pore diameter being one of them—do not assume unique values and are always distributed around one or more modes representing their averages. This is true even for single-particle materials, *viz.*, those composed entirely of particles of the same kind like carbon powder or platinum black, for there can be at least two effective radii indicating the nature of particle distribution and the particle composition. But many porous media used as electrodes have—on optimum-design consideration—differing pore-diameter structures linked together as, for example, in dual porosity models, thereby introducing another type of non-homogeneity. Further, with a view to

obtaining, certain required characteristics like non-wetting, conduction, etc., it may be considered desirable to include certain metallic or non-metallic agents like Pt. black or teflon in this process thereby making the nature of a real porous matrix much involved.

The reactants can be fed in the gaseous state or as species soluble in the electrolyte. Thus a porous electrode while operating has to contend with the phenomena associated with all the three phases and hence with the corresponding interfaces, since the electrochemical reaction is heterogeneous. Thus the *material* components of the system, *viz.*, the solid particles, the possible gaseous fuel, the electrolyte carrying the currents, etc., interact in a region whose geometry is complex and difficult to describe. To know the system performance, we have to know the *phenomenological* components as well (Table I). It is well known, for example, that: (i) the finite conductivity of the electrolyte and, in some cases, of the matrix as well, (ii) the finite rate of charge transfer reaction, and (iii) the mass transport of the reactants and products (and intermediates) can all cause the so-called polarisation effects, offsetting at least partly the advantages of employing porous electrodes. In other words, operating with a high specific surface area medium like the porous body creates its own problems. A limiting rate on the performance may result from any one of the above, *viz.*, the conductivity, velocity of the electrochemical reaction or rate of mass transfer being very small. Included in the above category are events like transport across gas/electrolyte interface, adsorption on solid surface, and diffusion or migration to catalytic sites on the surface of the metal. Hence, it follows that the information relevant to porous electrode operations like: (a) limiting current densities attainable, (b) regions that contribute effectively to the overall rate of reaction, (c) the potential distributions inside the electrode, etc., is closely related to the interplay of the phenomenological components outlined above.

2. An exact theoretical analysis of this system is rendered impossible mainly by the following factors; (a) the structural details of

TABLE I  
Porous electrode operations



the internal surface of the porous body are not known precisely, (b) the equations describing the mass transport and the potential variations are not only non-linear and multidimensional but are also simultaneous, and (c) the problem of defining the geometry of the three-phase boundaries—the so-called active regions—where the reaction rates may be significant; is similar to the uncertainty posed by (a) but of a different category. To circumvent the above, idealisations of various sorts are resorted to.

Firstly, the problem (a) suggests—at one end—that real structures may be idealised as parallel, cylindrical or of lattice-type (or similar ones with manageable symmetry) for purposes of theoretical analysis. On the other extreme, we find a completely statistical description also useful.

Secondly, to avoid the pursuit after solutions of multidimensional non-linear equations, a reduction in the number of dimensions (mathematical) is achieved by a clever, though suspicious, homogenisation. The third difficulty, *viz.*, the local geometry of the three phases (in contrast to the overall cell geometry or even macroscopic geometry of the porous media)—is again idealised. To sum up, attempts to avoid the cumbersome aspects of porous electrode operations, *viz.*, the porous structure, multidimensional equations and the multiphase geometry, have been three-pronged and the above three approaches may be judiciously combined to formulate models to explain the behaviour of porous electrodes.

3. Several models for describing the operation of gas-diffusion electrodes are now available and it is not surprising if many more are being studied. There are at least three reasons why such diverse models are currently studied. Firstly, the designs of gas-electrodes for a given set of operating conditions can be so different that a single model is unlikely to explain the operations of all these. For example, single and multiple-layer structures, apart from those with randomised distribution of micro and macro pores are currently in use. Why should one particular type of idealisation suit all these? Secondly, the electrochemically active regions of such gas electrodes are determined by the so-called three-phase boundaries with attendant uncertainties as regards the geometry, mode of transport of certain reactants to the reaction sites (and the removal of products) and the mechanism of the reaction in such a region. All these, in turn, suggest different types of approaches to this solution. Lastly, the operating regimes of such electrodes in terms of the parameters like temperature, pressure, the nature of the electrolyte, etc., can be so varied that a particular model may be unacceptable for a particular choice of these variables but still be valid under a different condition.

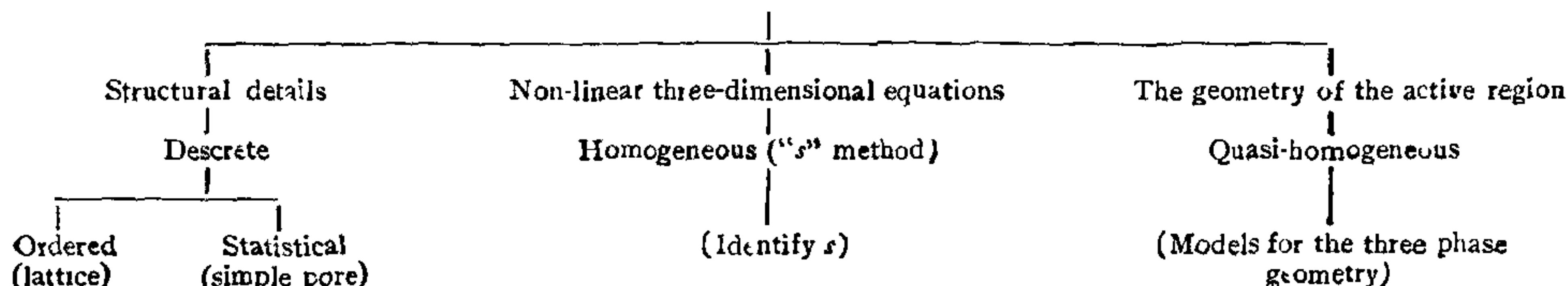
4. A classification of these models into several groups dictated by considerations such as those mentioned earlier may be attempted as follows:

- (A) Homogeneous;
- (B) Quasi-homogeneous; and



(C) Statistical or discrete models (see Table II). surface in the expression for the sources is understandable. With a three-phase system, one

TABLE II  
Theory of porous electrode operations



(A) A homogeneous picture of the gas-diffusion electrodes solves the multi-dimensional difficulties posed by the real system by reducing the number of space variables considered. In effect, this implies that we view the interconnected multi-phase system as a single homogeneous phase. This reduces the complexities of analysis enormously and provides us an insight into the phenomena. What the well-known homogeneous model for the flooded porous electrodes—the two-phase porous electrode/electrolyte system—does is to replace the distributed heterogeneous sources/sinks by appropriate homogeneous or volume entities. [See for example, E. A. Grens. II and C. W. Tobias, *Ber. Bunsenges. Physik. Chem.*, 68 (1964), 236, R. de Levie, *Adv. Electrochem., Electro Chem. Eng.*, 4 (1967).] A similar, direct, reduction of the three-phase gas-electrode/electrolyte problem to a flooded version can be done and hence a corresponding homogeneous picture emerges. In such an approach, we are not obliged to handle the structural details of the porous matrix directly nor is there a need to know the geometries of the active sites explicitly.

In the elementary flooded pore model, the homogenisation was more straightforward. This was achieved by assuming a local current density-potential relationship,  $i = f(\eta)$  and the transformation of the surface (amp/cm<sup>2</sup>) to volume (amp/cm<sup>3</sup>) sources (or sinks) was effected by replacing  $i$  by  $s \cdot i$  and setting up the relevant differential equations (the parameter  $s$  signifying the specific surface of matrix cm<sup>2</sup>/cm<sup>3</sup>). Such a procedure is easy to comprehend as the electrochemical reaction takes place (though with different rates) along the entire (internal) surface (of the porous medium) and hence the presence of the specific

may still introduce  $s$  as was done earlier in the flooded-porous medium but its meaning is less precise now since we may not be able to identify it with the total internal surface. The interpretation of  $s$  is closely linked with our description of the reaction mechanism. Homogeneous models with the following variations have been proposed for the gas-filled electrodes:

- (Aa)  $s$ : total internal electrode surface—same as in the flooded-porous model—this description is expected to be fairly accurate for gas content of the order of 80%: O. S. Ksenzhak.
- (Ab) *Macroporosity*: internal surface of wide pores—valid if wetting of macropores by a film of electrolyte is possible: A. G. Pschenichnikov.
- (Ac) *Common area* between the gas and liquid; this may be evaluated if the pore-distribution statistics are known: V. S. Markin et al.

[Refer *Fuel Cells—Their Electrochemical Kinetics*. Ed. V. S. Bagotskii and Yu. B. Vasilev, Consultants Bureau (1966), New York.]

In all the above, the parameter  $s$  is a body-characteristic that may depend upon the gas pressure via  $r_c$ , the critical radius that decides which of the pores will be flooded. More generally,  $s$  may be any empirical parameter that is capable of being defined a priori in terms of the structural and equilibrium properties of the porous medium alone. It follows therefore that for analysing gas-electrode operations through the above models, we can use the same mathematical apparatus studied in detail for the flooded-porous systems except that different meanings may have to be attributed to some of the parameters. Moreover, once the relationship of the constants like  $s$  to the struc-



ture properties are made explicit as in A(a)–A(c), the mathematical solutions are well-poised for being verified for their predicted dependence on structure constants and variables like gas pressure, etc.

5. (B) The second class of models, viz., quasi-homogeneous attempt to simplify the problem stagewise. Firstly, the regions (active) as regards the electrochemical reaction and the geometry of the three-phase region are idealised. Appropriate equations are formulated keeping in view the details of the mass and charge transport associated with the proposed geometry and the reaction mechanism. A solution of these equations gives us, then, the local strength of the sources/sinks. This is carried over properly to be imbedded in a homogeneous model, incorporating also the phenomena of mass and charge conduction in the rest of the porous body. Essentially, therefore, the two stages in this modelling are: (i) a model for the three-phase boundaries and the phenomena occurring therein, and (ii) relating the results of (i) to the results concerning the porous body via homogenisation and a knowledge of the overall distribution of such boundaries. Variations in this class of models arise due to the plurality of descriptions possible in both (i) and (ii). The structure of the three-phase region and the impact of this on the potential or activity distributions therein have been the concern of many workers. But, compared to this, the methodology of transforming these results to the real problem of obtaining results for the porous body has engaged much less attention. [For an outline of some of the three-phase geometries, refer: *Fuel Cells and Fuel Batteries*, by H. A. Liebhafsky and E. J. Cairns, Wiley. (1968), and *Fuel Cells—Their Electrochemistry* by John Bockris and S. Srinivasan, McGraw-Hill (1969).]

6. Another ideal approach lies in not ignoring the structure as in the previous approaches but in idealising it. Two elementary models falling under this classification are:

- (a) Single-pore approach, and
- (b) Lattice or cell method.

(a) The former assumes non-intersecting pores as constituting the system and assumes at least two parameters  $r$  and  $\delta$ .  $r$  denoting the radius of a typical solid capillary and the other, viz.,  $\delta$  as a distance-parameter representing the packing of such solids. The exact boundary value problem is then solved taking into account the geometry of the pores and its environment. The results deduced for this

model will no doubt be functions of  $r$  and  $\delta$  and the averaging over the proper ensemble leads to the results relevant to the overall medium. The methodology is pseudo-deterministic and can be expected to yield at least a qualitative solution to the problem.

The complementary case, viz., non-connected cylindrical voids imbedded in a solid matrix, is well known and is simpler. This approach may be useful while one wants to study specific pore size effects like those of varying thickness, etc.

(b) The cell or lattice model is especially useful for studying an interconnected pore-medium. In its simplest form, this too depends on two parameters as the single-pore approach but should be viewed now as some sort of a cascade process where each unit cell alters the flux that should be fed on to the next. As before, there is always a probabilistic factor involved in these arguments and should not be lost sight of.

The above two approaches represent the two extremes of the spectra of possible designs for porous matrix. To the author's knowledge, more investigations on these lines are needed. (This is not to be confused with the structure-model-approach which defines the capillary equilibrium or relates effective parameters like  $r_p$ ,  $s$ , etc., to the structure. What we imply here is a complete discretisation, i.e., that which includes the mass transfer effects, etc., also.)

7. From what has been examined in this paper thus far, a few questions emerge:

(a) If the mathematical modelling does not bear a one-to-one relationship with the physical nature of the phenomenon, how do we compare the models? When are these pictures distinct and when do they merge with each other?

(b) Is it possible that new models may be postulated, improving (or disproving) the earlier ones as evidenced through the experimental results with, let us say, the oxygen electrodes?

(c) Though the detailed structure of the porous medium is ignored in the models, certain appropriate system parameters are introduced to account effectively for this deviation from reality. How are these effective parameters dependant on the porous structure? For example, what can be said of the structure of the interphase boundaries (liquid-gas) inside the porous body or of the capillary equilibrium?



(d) What are the perspectives as regards the types (and the design) of electrodes and the techniques to be employed in such studies? These questions were taken up during a recent symposium organised by the SAEST at Karai-kudi.

(a) S. K. Rangarajan, besides reviewing critically the present state of the theory of porous electrodes, presented some results concerning the application of comparison theorems to the non-linear equations arising in this topic and also the transient analysis of such systems.

(b) K. Micka (Heyrovsky Institute of Polarography, Prague) presented experimental results to substantiate his model of porous electrodes of second order that considers, apart from the usual two systems of pores (larger gas-pores and smaller flooded-pores), very fine pores due to the catalyst particles and flooded with electrolyte.

The problem of relating the local current density potential relationship (micro-kinetic) to the experimentally accessible current-potential curves (macro-kinetics) in the flooded porous system, assuming limitations due to the mass transfer of the reactants and products was discussed in detail by I. G. Gurevich (Heat and Mass Transfer Institute, Minsk, USSR).

(c) The statistical aspects of the capillary equilibrium as a basis for test of models was considered by Yu. A. Chimadzhev (Academy of Sciences, USSR).

(d) M. Bonnemay and G. Bronoel (Laboratoire d'electrolyse du CNRS, France) discussed

about the triple contact electrodes and the possible future role of dispersed or suspension electrodes in electrochemical power sources. The need to tackle urgently the problems of education, training (and attitude) and needed directions in basic research as well as perspectives on the future of electrochemical energy conversion and storage were stressed by J. O. M. Bockris in his address (Tables III and IV).

TABLE III

(due to J. O. M. Bockris)

*Some peculiar priorities (1969 \$ millions)*

Battery Research—All U.S.	..	5
Fundamental Electrochemistry—Research	..	1
G.M. Anti-Pollution Research	..	8
N.A.P.C.A. Total Budget	..	112
G.M. Advertising	..	240
Model Change, Car Companies	..	2000

TABLE IV

(due to J. O. M. Bockris)

*Some peculiar priorities  
(Ph.D.'s per year)*

All Chemistry	..	c. 2000	(U.S.)
Electrochemistry (1969)	..	5	(U.S.)
		10	(U.K.)
		26	(Germany)
		52	(U.S.S.R.)*

\* Equating Kandidat degrees to U.S. Ph.D.

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## SOIL-BASED IRRIGATION FOR MAXIMISATION OF CROP YIELDS WITH A GIVEN UNIT OF WATER

C. DAKSHINAMURTI AND D. SUBBARAMI REDDY

*Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi, India*

IT is well known that over 35% of the irrigated lands of the world have either turned saline or alkali, due mostly to injudicious irrigation and inadequate drainage (Dakshinamurti, 1962). Irrigation water has become a precious commodity all over the world, more so in the tropics and developing countries. Although extensive investigations have been carried out on the irrigation requirements of crops, the concept has all through been in supplying certain quantities of water based mostly on the agronomic observation of the water requirements of crops. The water-holding capacity of

the soil which plays an important role in preserving the water and supplying it to the user—the plant, has never been kept in mind. This resulted mostly in the loss of water by percolation and leaching of nutrients from the soil. It is, therefore, thought desirable in the present investigation to find out the amount of water held in the first 30 cm of the root zone at the field capacity and give new concept to the quantum of irrigation water given per hectare.

Two promising varieties of wheat, namely, Sarbati Sonara, a two gene dwarf and I.I.D.