pendent upon the potential difference across the metal-solution boundary. This topic and its applications are discussed under: definition, basic concepts, present structure, recent advances, directions of future research, applications. One table, 9 figures and 23 references.

—T.L.R.

(B) Batteries and Fuel Cells

1. Electrode phenomena of silver-silver oxide system in alkaline battery—

S. Yoshizawa and Z. Takehara (J. Electrochem. Soc., Japan, **31**, No. 3, 91, 1963). Electrolytic behaviour of the silver-silver oxide system in an alkaline battery and effects of addition of various metals to the silver electrode were studied by utilizing electron-microscope and x-ray diffraction methods and oscilloscopic technique for the determinations of decay and growth of overpotential and current-potential relations. It was shown that during charge, silver oxide, and silver peroxide were successively found followed by the expansion of silver crystal owing to a diffusion of oxygen ion; on discharge, the reverse process should be occurred.

2. Electrochemical oxidation of methane in phosphoric acid fuel cells at 150° C—

W. T. Grubb and C. J. Michalske (Nature, **201**, 287, 1964). In fuel cells operating below 100°, methane was inert. In fuel cells at 150°, with porous platinum electrodes, methane was quite reactive when the electrolyte was orthophosphoric acid 14.6 molar or 85 weight per cent. At current density less than or equal to 20 mA/cm² the cell performance with methane was better than with propane. Gas chromatographic determination from methane-oxygen cell showed a carbon dioxide yield 98 ± 4 per cent that required by the anode reaction. The methane platinum black anode in orthophosphoric acid at 150° sustains a steady state current density of 48 mA/cm² only, 0.5 v. from the reversible hydrogen potential in the same electrolyte.

3. Thermally activated power cells—

B. W. King et al. (American Ceramic Society Bulletin, **43**, 117, 1964). Austin cells consisting of layers of dissimilar etals with an intermediate layer of glass were investigated and found to be galvanic cells. They are thermally activated in the sense that as the temperature is raised the internal resistance decreases rapidly and the (power) output increases. The cells investigated generated power by the oxidation of one metal layer. The other metal served essentially as an electrode. Glass or porcelain enamel served as an electrolyte, or ionic conductor. The cell potential was closely related to the energy of oxidation of the metal consumed. Several type of cells were prepared and their characteristics measured.

4. Fuel cells, a state-of-the-art report—

R. J. Jasinski and T. G. Kirkland (Mech. Engg., **86**, No. 4, 121, 1964). Various applications — space, terrestral are discussed. Further the article deals with the efforts abroad, together with research efforts regarding catalysts and electrode structures.

5. Further studies on plante plate formation using nitrate as forming agent—

Miss R. Vijayavalli, P. V. Vasudeva Rao and H. V. K. Udupa (J. Electrochem. Soc., India, **13**, 7, 1964). Plante plate formation for stationery lead-acid batteries using nitrate as forming agent has been described. The role of formic acid and urea were re-examined and their addition was found to be having no special advantage. Formation using only nitrate as addition agent could give plates which gave capacity as per IS specification. Shedding was observed to be low during cycling. 30 A.H. plates were formed, and their capacities determined. The performance characteristics conformed to the IS: specification for these plates.

6. On the use of gold reference electrodes in fuel cell studies—

R. Thacker and J. P. Hoare (Electrochemical Technology, **2**, 61, 1964). It has been shown that a small anodized gold bead at the end of a gold wire may be used as a micro-reference electrode in single-electrode fuel cell studies. In basic solution, a potential between 950 and 1100 mv vs platinum/hydrogen in the same solution is obtained. The potential of such an electrode must be calibrated periodically against a saturated calomel electrode. In acid solution, a very stable and highly reproducible electrode having a potential of 1.360 ± 5 mv./vs normal hydrogen electrode may be from a slurry of the auric oxide in the acid solution. The polarization data obtained on a fuel cell air electrode in 8N potassium hydroxide using a gold bead micro-reference electrode are presented. The oxygen overvoltage measurements agreed with similar data in the literature.

7. **Hydrocarbon fuel cells with invariant electrolytes—**

E. J. Cairns and D. I. Macdonald (Electrochemical Technology, **2**, 65, 1964). Cesium and rubidium carbonates and bicarbonates in aqueous solution have been found to be suitable invariant electrolytes for organic fuel cell operation at temperatures up to 200° C at atmospheric pressure. Fuel cell experimental evidence shows that these electrolytes support essentially complete electrochemical oxidation of ethylene, methanol, ethane and carbon monoxide when platinum black is used as the anode. No performance degradation was detected after 200 hr. of fuel cell operation. The products of catalytic dehydrogenation and cracking reactions on the anode can greatly influence the fuel cell performance. A high-efficiency hydrocarbon fuel cell may require a methane utilizing anode. A new fuel gas circulation system is described.

8. **Gaseous fuel cells—**

K. R. Williams and D. P. Gregory (U.S. 3, 116, 170, 1963; C.A., **60**, No. 10, 11622b, 1964). A method of producing gaseous fuel cells having electrodes made by depositing a specific amount of conductive material on a porous non-conductive substrate having a pore size of specific diameter is described.

9. **Process for storage of electrical energy—**

Helmuth Mylius (Ger. 1, 161, 966, 1964; C.A., **60**, No. 10, 11622c, 1964). A device for storing electrical energy is described by using ferrous/ferric oxidation-reduction system with a complex catalyst. The cell has bipolar graphite electrodes, anode and cathode compartments are separated by a semipermeable polyethylene diaphragm. For example, the electrolyte contains six parts ferrous chloride, ten parts water plus catalyst containing 0.1 per cent titanium chloride, 0.01 per cent aluminium chloride and 0.075 per cent boric acid (all percentages calculated on basis of ferric chloride content) β—Aminopropionic acid (0.002 per cent is added in some examples). The catalyst overcomes the disadvantages of uncatalyzed system.

10. **Electrodes and method for making the same—**

J. C. Duddy (U.S. 3, 121, 029, 1964; C.A., **60**, No. 10, 11622cd, 1964). Electrodes were prepared from platinized mixture of by weight, 1 part ploye thylene and 1-3 parts polyethylene oxide as permanent and temporary binder, and either one of in parts by weight, cadmium oxide, 28, silver 22, silver oxide 7, litharge 37, zinc oxide 37, stannic oxide 14, antimony trioxide 20, green nickel hydrate 1.38 + graphite 3.2, yellow HgO 20 + graphite 2.4, copper oxide 10 + graphite 0.68, or manganese dioxide 10 + graphite 1.7. The mixture was calendered to sheets and pressed on nickel grids. Electrodes were cut and the polyethylene oxide dissolved in water. A nickel electrode thus prepared 1.75 x 2.25 x 0.026 in., charged in 31 per cent potassium hydroxide, and having only 2/3 the wt. of a conventional sintered electrode, on discharge to 0.6 v. with 0.25 amp/sq. in. gave 0.22 amp. hr./g. nickel hydroxide or 76 per cent efficiency.

11. **An electrode for an electric cell or battery—**

(Brit. 948, 745, Feb. 1964; C.A., **60**, No. 10, 11622f, 1964). Porous microcrystalline deposit of electro-chemically active metal, such as zinc, cadmium or silver is electrolytically deposited on a carrier and then mechanically densified. A zinc electrode was prepared from the following plating bath; 30 per cent potassium hydroxide and 5 per cent zinc oxide in water. Anodes-zinc balls and cathodes-copper sheets, operating conditions: plating voltage 1.85-2.25 v; temp. 25°C; discharge current densities, 15-25 amp/dm² (cathodic). Cadmium electrodes prepared from a bath containing 25 per cent ammonium chloride, 5 per cent cadmium oxide, and 6 per cent hydrochloric acid gave discharge rates of 1.5-3.0 amp/dm². Silver utilizations to 2.0 g/amp. hr. were obtained from silver electrodes similarly processed from a bath containing potassium hydroxide 25, silver cyanide 5, potassium cyanide 1.5, and potassium carbonate 2 per cent.

12. **Alkaline storage battery cell—**

(Ger. 1, 160, 909, Jan. 1964; C.A., **60**, No. 9, 10221b, 1964). The positive electrode of the cell consists of mercuric oxide and a conductive mixture of powdered silver and finely divided graphite (or) active charcoal, the mercuric oxide content preferably being 50-70 weight per cent. The negative electrode may contain 1-5 weight percent toluic acid, terephthalic acid, or isophthalic acid.

13. **Method of manufacturing electrodes for fuel cells, cells or batteries—**

J. C. Duddy (U.S. 3, 120, 457, Feb. 1964; C.A., **60**, 9, 10221c, 1964). Silver oxide pow-

der is mixed with an insoluble thermoplastic resin such as polyethylene (8-20 silver oxide + 1 resin). Powdered metal, such as silver, platinum, etc., is mixed with soluble resin such as polyethylene oxide. The latter is mixed with the original metal mix to form the electrode by molding extrusion, etc. The soluble resin is leached out by a suitable solvent. The electrode may be structuralized by sintering.

14. **Sealed alkaline storage battery with a hydrogen absorbing electrode—**

(U.S. 3, 117,033, Jan. 1964, C.A., **60**, No. 9, 10221g, 1964). In a hermetically sealed alkaline storage battery, there are, in combination, positive and negative electrodes, an absorbent separator between the positive and negative electrodes, and alkaline electrolyte substantially absorbed by the electrodes and separator, and a gas consuming auxiliary electrode containing Ag or Ag compounds connected electrically with the positive electrode and located at the side of the positive electrode which faces away from the negative electrode. The connections formed by the alkaline solution and the metallic connections between the auxiliary and positive electrodes allows the Ag in the auxiliary electrode to be converted to hydrogen absorbing silver oxide. Additional auxiliary electrodes may be used.

15. **Sulphur dioxide-sulphur trioxide fuel cell research—**

(E. L. Kumm. NASA Doc. N62-17.308, 1962; C.A., 60, No. 7, 7673c, 1964). The thermodynamics and electrolytic characteristics of a sulphur dioxide-sulphur tiroxide regenerative, closed-cycle fuel cell are discussed, and various aspects are studied to determine the practicability of uch a fuel cell. Widely varying experimental results proved such a fuel cell is not feasible.

16. **A comparison of silver-cadmium and nickel-cadmium batteries for use on the transit satellites—**

W. E. Radford (NASA Doc., N62-10.142, 1962; C.A., **60**, 7, 7673d, 1964). A silver-cadmium battery can store twice as much power per unit wt. as the nickel-cadmium battery now used in transit satellites. Investigations have proven the compatibility between silver-cadmium batteries and solar cell charging devices; silver-cadmium cell voltage is fairly independent of cell temp.; these cells in combination with solar cells are able to limit overvoltage current.

17. **Air regeneration of bromine-bromide fuel cell catholyte—**

W. E. Reneke (U.S. Dept. Com., Office Tech., Serv., AD273, 299, 1961; C.A., **60**, No. 7, 7673f, 1964). By using the existing data and data taken from the operation of the column, a packed column for the regeneration of bromine from hydrogen bromide was designed. The estimated size was very large in relation to the power it would be expected to supply: a packed tower was not suitable for this purpo e. A closed system using high concentrations of nitric oxide and supplied with pure oxygen would be suitable means of regenerating bromine from hydrogen bromide.

18. **Design and development of hydrogen-oxygen fuel cell power—**

H. J. Latimer, et al. (NASA Doc., N63-22142, 1962; C. A., **60**, No. 7, 7673g, 1964). A sliding vane design wa us d for the hydrogen circulating pump in order to lower parasite power consumption. Automatic operation of a power plant was achieved with all parasite loads supplied by the fuel cell. This led to the substitution of operation of two power plants in parallel (elec.) for 50 hrs.

19. **Electric cell—**

S. Zaromb (U.S. 3, 114, 658, December 1963; C.A., **60**, No. 7, 7682, 1964). An electric cell is described which can be recharged by application of an electric current or exposure to sunlight or ionizing radiation. A two-compartment cell is used with a light-sensitive silver halide membrane serving to divide the cell. In one construction the positive electrode is a platinum screeen in 0.1M hydrochloric acid, while the negative electrode is porous carbon in a solution of 0.02M hydrofluoric acid, 0.05M ferric chloride and 0.01M ferrous chloride. The cell membrane is silver chloride which can be irradiated by light.

20. **Fuel cell and fuel cell electrodes—**

C. E. Thompson (U.S. 3, 116, 169, 1963; C.A., **60**, No. 7, 7682e, 1964). A fuel cell is described in which cobalt molybdate is used as a fuel electrode catalyst and depolarizer. In practice the cobalt molybdate is impregnated in a porous carbon electrode. It can be used in cells where electrolytes are acids, bases, or carbonate solutions. Cell temperature range is 77 to 600°F. The catalyst is superior to those previously available when fuels are hydrogen or combustible organic compounds.

21. **Coupled distribution of voltage and concentrations in electrochemical cells—**

M. Guillou (Ann. Phys., **8**, No. 10, 1963). The study of a channel electrode led to a qualitative understanding of the distributions of electrochemical activity in an electrode, and employed rheographic experimental methods which may be useful in solving Laplace problems.

22. **Use of palladium hydrogen diffusion electrodes in fuel cells—**

N. Busson, et al. (J. Chim. Phys., **60**, 11-12, 1355, 1963). The influence of chemical and thermal treatment of thin layers of palladium on hydrogen diffusion at ambient temperature is studied with possible use of palladium electrodes for fuel cells in view. The conclusion is that palladium electrodes will not be useful in low temperature fuel cells using alkaline electrolytes.

23. **Fuel cell I. Fundamental research on hydrogen-oxygen cell—**

N. Sakikawa, et al. (Kogyo Kagaku Zasshi, **66**, No. 8, 1178, 1963). The polarization characteristics of a hydrogen-oxygen fuel cell were studied especially on the structure of the electrode. Granules of activated carbon were piled in a glass tubing with a sintered glass bottom, and used as electrodes. Another type of electrode was activated by palladium or by platinum. The voltage obtained was 0.9855V (10°) in 40 per cent potassium hydroxide solutions and the optimum temperature was 70°. The polarization characteristic was much improved by coating the electrode with silicone resin.

24. **Fuel cell II. Fuel cells with methanol as fuel—**

N. Sakikawa and A. Kuroda (Kogyo Kagaku Zasshi, **66**, No. 8, 1182, 1963). A new type of fuel cell using methanol at high temperature was studied. A copper pipe plated with nickel was used at 100-200° as the electrode, and the oxygen electrode was porous carbon plated with silver. Methanol was used as fuel, and the electrolyte potassium hydroxide was dissolved in it. The electrode reaction was controlled by the hydrogen formation due to the thermal decomposition of methanol at the heated electrode surface. The major disadvantage of the cell of this type was the bad contact of methanol with the electrode surface at the high temp.

25. **Fuel cell III. Fuel cells with alcohols in liquid phase—**

N. Sakikawa, et al. (Kogyo Kagaku Zasshi, **66**, No. 8, 1186, 1963). Fuels cells using alcohol as the fuel at low temp. had electrodes of Pt black. The oxygen electrode was porous carbon plated with silver. Alcohol as fuel was dissolved in potassium hydroxide solution. Formaldehyde formed by the oxidation of the fuel showed good discharge characteristics, while formic acid was poisonous. The optimum temperature was approximately 60°.

26. **Behaviour of β-manganese dioxide after heating to 350-450° in galvanic cells of the Leclanche type—**

C. Drotschmann (Batterien, **17**, No. 11, 574, 1964). The findings of Appelt that heat treatment at 350-450° of β-manganese dioxide distinctly increased its capacity in special test cells at continuous discharge could not be verified with Caucasian β-manganese dioxide in standard Leclanche test cells.

27. **The influence of the character of the manganese dioxide on the discharge process in the Leclanche dry cell—**

Heinz Harnisch and A. Mehne (Elektrotech. Z., **84**, No. 22, 723, 1963). Synthetic manganeze dioxide is ppted. from a solution of manganese chloride or sulphate by addition of a sodium hydroxide-sodium hypochlorite solution. Physical and chemical properties vary with conditions used for precipitation and work-up. Cells are prepared by using electrolytic or synthetic manganese dioxide are discharged over resistances of 25-250 ohms. Plots of voltage vs. discharge time show the effect of other variables. Properties related to diffusion processes within the bobbin are most significant. Manganese dioxide prepared from manganous salts is superior to that obtained as a by-product from saccharin production.

28. **Thermodynamic properties of electrochemical storage cells—**

M. I. Gillibrand and B. E. Wilde (Electrochim. Acta, **9**, No. 4, 401, 1964). The heat evolved when lead/acid electrochemical storage cells are charged and discharged in an adiabatic calorimeter was detd. The heat content change and the free-energy change for the electrical storage capacity of the cell are calculated

from the results. These values are the same as have been previously established from e.m.f. measurement for the equil. reaction in the cell. Similar calorimetric measurements were made with nickel-cadmium alkaline cells, in which equil. conditions cannot readily be obtained. The heat-content change and free-energy changes for the reactions which account for the elec. capacity of this system are 32.9 kcal/F and 30.1 kcal/F. resply.

29. **Studies of the decomposition of active materials at the cathode of nickel-cadmium accumulators—**

J. P. Harivel and J. F. Laurent (Electrochim. Acta, 9, No. 6, 703, 1964). The several oxidation states obtained during the formation of nickel oxides at different rates of charge and their stability in the presence of or absence of foreign ions in the lattice, are compared by a method based on the decomposition of these oxides in aqueous media, based on the time of immersion of an oxidized electrode in a reducing solution. The reduction rate is first order, and rate constants are evaluated at different temperatures as functions of the extents of oxidation. Activation energies are calculated and oxides formed during electrochemical oxidation can be estimated from the activation energies.

30. **Study of a graphic-oxygen high temperature fuel cell—**

F. R. Duke and J. C. Copelan (U.S. At. Energy Comm. IS-665; C.A., **60**, No. 5, 6473fg, 1964). Electrolytic cells of type C (graphite)/CO_2 (g) electrolyte/O_2 (g), Pt were studied at about 800°. Electrolytes used were sodium molybdate-molybdic anhydride, sodium tungstate-tungstic oxide and borax-boric oxide. Cell construction and cell reactions described. Localized supersaturation, which was not localized, is responsible for the descrepancies. The temp. dependance of e.m.f. for the tungstate system studied at 739-869°. Slope and standard entropies evaluated. The highest e.m.f. attained corresponds to an error of 10.8 per cent of the theoretical E° value. The borate system shows the greatest promise for fuel cell application.

31. **Kinetic basis for the opening of sealed nickel-cadmium cells—**

U. B. Thomas, Jr. (Proc. Intern. Battery Symp., 3rd Bournemouth 1962, 117, 1963). Equations for discharge and charge of nickel-cadmium are tested for agreement with net changes in water and potassium hydroxide content of the electrolyte during cycle. Limitations of total electrolyte discussed. Formation of oxygen is of first order and limited by rate of transport. Adequate negative charge reverse prevents hydrogen evolution.

32. **Fuel cell electrodes—**

A. J. Hipp (U.S. 3, 116, 165, Dec. 1963; C.A., 60, No. 6, 6489c, 1964). Satisfactory electrodes are produced by coating nickel with platinum and palladium. Detailed procedure described.

33. **Gas electrode in fuel cell—**

C. E. Tirrel (U.S. 3, 117, 034, 1964; C.A., 60, No. 6, 6489f, 1964). A fuel electrode assembly contains a flexible sheet-like macroporous non-metallic fiber support, such as acid-leached asbestos, consisting a relatively acid-inert material impregnated with graphite or interwoven with graphite fibers, also impregnated with a platinum group catalyst. This gas-permeable electrode, together with a second electrode constitutes a fuel cell.

34. **Porous electrodes for alkaline storage battery cells—**

L. Schlecht, et al. (Ger. 1, 159, 528, Dec. 1963; C.A., **60**, No. 6, 6489f, 1964). Porous electrodes for alkaline storage battery cells are made by sintering metal powders obtained by mixing two different foms of powdered metal, e.g., nickel, preferably nickel powder is used, which has been obtained by thermal decomposition of nickel carbonyl in a heated free space.

35. **Ion exchange membrane properties — their effect on the development of the dual membrane fuel cells—**

R. M. Lurie, et al. (J. Electrochem. Soc., **110**, 1173, 1963). Dual ion exchange membrane fuel cells consist of 2 membranes separated by a liquid layer, and are supposed to be cationic. The construction, performance and life test data are given. This construction has the advantage over cells wih a single membrane of using a larger number of aqueous or nonaqueous electrolytes, of greater temperature, stability, resistance to hydration, and greater safety from explosive mixing of hydrogen and oxygen.

36. **Possibility of utilizing decomposition energy of sodium amalgam in a fuel cell—**

J. Przyluski and R. Batijawski (Prezemysl Chem., **42**, No. 11, 624, 1963; C.A., **60**, No. 5, 5069a, 1964). A liquid sodium amalgam electrode was constructed that operates at 20° with 0.25 per cent sodium content of amalgam and 920 amp./m². At 70° and 1300 amp/m² complete decomposition of amalgam resulted with 2N sodium hydroxide as electrolyte.

37. **New organic depolarizers—**

E. A. McElhill, et al. (Proc. Ann. Power Sources Conf., **17**, 145, 1963). Over 200 organic compounds containing various reducible groups were tested for depolarizer activity in a specially designed half-cell. As the reaction proceeds the loss of cond. of electrolyte or pore plugging of cathode by bulky products overshadows the structural advantages of individual deplorizers.

38. **Mechanism of the processes in a silver electrode of a STS storage battery—**

V. N. Flerov (Zh. Prikl. Khim, **36**, No. 9, 1980, 1963; C.A., **60**, No. 5, 5069,g, 1964). The charge and discharge characteristics are evaluated and found to be a function of the anodic processes, the current density, temp., interruptions, the duration of storage before the beginning of discharge, and the number of cycles. The peculiarities of the Ag electrode were interpreted in terms of a solid-phase mechanism on the upper plateau and on the possibility of aging of the oxide phase.

39. **Action of separators on the migration of antimony in lead-batteries—**

F. Zehender et al. (Electrochim. Acta, **9**, No. 1, 55, 1964). In storage cells of practical design, a boundary region free of separators is put in parallel to the separators. When studying the effect of this boundary region it was found that it affects little the antimony migration in the case where mediocre or bad separators are used but that it limits the action of good separators..

40. **Fuel cells — a state of — the art — report—**

R. J. Jasinski, and T. G. Kirkland (Mech. Engg., **86**, No. 3, 51, 1964). In this article, a broad classification into hydrocarbon and non-hydrocarbon fuel cells is made. Under each head different varieties of fuel cells, are described and discussed. Further, regenerative and non-regenerative fuels are described, exemplifying each item.

—D. V. S.

(*Concluded from Page* 60)

burned in the generator which produces an electric current sufficient to cathodically protect the pipeline. The cost of this current at present is about £ 9 per watt—Corrosion Technology, Vol. 11, 11, 1964.

Challenge in Materials Engineering

A report of a round table discussion in Metal Progress, June 1964 brings out forcibly the close relationship of materials selection to manufacturing processes. The metal-working properties of a material—its forming, machining, joining, heat treating and finishing characteristics—are of great concern to the materials engineer in this competitive age. Further, the great range of engineering components required today and the demand for higher strength materials in many applications present problems which can be solved only by integration of the materials selection and processing functions. The challenge is clear: today's materials engineer must make recommendations and decisions that are compatible with the objectives of the designer, yet which keep the practical aspects of producibility in mind.

—T. L. R.