volved in a successful application of ion exchange in extractive metallurgy are presented in relation to several new promising processes such as magnesium from sea water, gold from cyanide solutions and lithium from spodumene. Three figures and 31 references.

34. **The application of nuclear energy to power desalination processes**—

J. B. Clampett (Australian Chem. Engg., **5**, No. 6, 9, 1964). This paper discusses the nature of the input energy to several of the more important desalting processes including electrolysis, and indicates the possible methods of using the energy available in nuclear fuels to power such processes. Four tables including economics, 10 figures and 7 references.

35. **Chemical activation**—

B. S. Rabinovitch and M. C. Flowers (Quarterly Reviews, **18**, 122-168, 1964). Review with 104 references: general characteristisation, survey of occurrence, and specific studies of chemical activation.

—T.L.R.

(B) Theoretical Electrochemistry

1. **The mechanism of electrochemical oxidation of carbon monoxide and methanol on platinum. The reactant-pair' mechanism for electrochemical oxidation of carbon monoxide and methanol**—

S. Gilman (J. Phys. Chem., **68**, No. 1, 70, 1964). The 'reactant-pair' mechanism assumes that the activated complex in the loss of the first electron from carbon monoxide involves an adsorbed carbon monoxide molecule adjacent to an adsorbed water molecule. A similar mechanism may be involved in the electrochemical oxidation of methanol in the acid solutions and other simple organic molecules at the lower range of overvoltages.

2. **Bivalent thallium and the mechanism of the electrode reaction $Tl^{a+} + 2e \rightleftarrows Tl^{+}$.**—

H. A. Catherino and J. Jordon (Talanta, **11**, No. 2, 159, 1964). Conclusive evidence is presented that the electrooxidation of the aquo monovalent thallium ion and the electroreduction of tervalent thallium ion proceeds via a bivalent thallium species. In molar aqueous perchloric acid the rate of the disproportionation process, $2Tl(II) \rightarrow Tl^{+} + Tl^{a+}$ is relatively fast compared to the electron transfer steps, $Tl(II) + e \rightarrow Tl^{+}$ and $Tl^{a+} + e \rightarrow Tl(II)$.

3. **Electrolytic formation of insulating oxide films on zirconium. Electrode kinetics at constant voltage**—

G. C. Wills, G. B. Adams and P. Van Rysselberghe (Electrochim. Acta, **9**, No. 1, 93, 1964). The kinetics of formation of insulating oxide film on zirconium electrode at constant voltage were used to test two theoretical expressions, Mott-Cabrera and Dewald theories, for metal oxide film formation kinetics. Interfacial and internal barrier heights and half jump distances were calculated. Some evidence is presented for variation of the concentration of metal surface active sites with film formation rate.

4. **Elucidation of the mechanism of electrolytic hydrogen evolution by the use of H-T separation factors**—

J. O'M Bockris and S. Srinivasan (Electrochim. Acta, **9**, No. 1, 31, 1964). Tafel parameters and H-T separation factors were determined on various metals in acid and alkaline solutions. The slopes greater than 2RT/FV are due either to adsorption of organic compounds or to the presence of conducting films. The mechanisms indicated are slow recombination on platinum and rhodium in acid solution, slow electrochemical desorption on copper and nickel in acid and platinum in alkaline solutions, slow discharge-fast-recombination on nickel and tungsten in alkaline solution, linked discharge-electrochemical desorption on mercury, lead (discharge rate determining) and cadmium (electrochemical desorption rate determining).

5. **Some theoretical considerations of quasi-reversible and irreversible electrode reactions in oscillographic square-wave polarography**—

Koichi Okamoto (Bull. Chem. Soc. Japan, **36**, No. 11, 1381, 1963). The magnitude of the transfer coefficient and reaction rate influence the polarographic wave of quasi-reversible reaction. The theoretical equations of irreversible waves in the cathodic and anodic sweep processes have been derived. The wave height of the irreversible electrode depends on transfer coefficient and is much lower than that of the reversible reaction.

6. **Kolbe electrolytic synthesis. Theoretical investigation of the mechanism by standard potential calculations**—

L. Eberson (Acta Chem. Scand., 17, No. 7, 2004, 1963). At the critical potentials may be discharge of $RCOO^-$, a chemisorbed layer of R is formed and mechanism of oxygen evolution is changed and the magnitude of oxygen overpotential is increased. At less nobler metals than platinum and iridium, the critical potential is not attained as the overpotential is low due to formation of oxide films. The standard potentials for primary and secondary reactions and the common rate constants at these potentials for forward and backward reactions were calculated. The empirical equation fit best the assumption of an irreversible one electron transfer with simultaneous breaking.

7. **Anodic oxidation of cadmium in concentrated alkali solutions**—

A. V. Fortunatov and L. A. L'vova (Zh. Fiz. Khim., 37, No. 8, 1712, 1963). A plateau of log i at ϕ=—0.85V is exhibited by all log i/ϕ plots. This is associated with the passage of ϕ through the null point charge. There was a sharp increase in the rate of oxidation during the transition from negative charged to the positive charged surface. The cadmium electrode possess adsorptive capacitance. Oxidation of cadmium in concentrated alkali solutions was governed by the reaction of hydroxyl ion with the surface of the cadmium electrode.

8. **Autopassivation of titanium in acid, neutral, and alkaline media**—

N. D. Tomashov and R. M. Al'tovskii (Korroziya Metal. Splavov, Sb. 141, 1963). The self-passivation of titanium takes place in solutions of sodium chloride, sodium hydroxide and in hydrochloric acid less than 1 per cent and sulphuric acid less than 0.33 percent even in the absence of oxygen. It can only take place in hydrochloric acid greater than 1 per cent and sulphuric acid greater than 0.33 per cent and in the presence of oxygen in the atmosphere, and in the electrolyte. The dissolved oxygen in the electrolyte acts as a cathodic depolarizer thus facilitating autopassivation.

9. **Electrochemical oxidation of formic acid**—

R. Slott (U.S. Dept. Com. Office Tech. Serv., AD 401, 932, 169 pp. 1963). Experiments were carried out to determine the effect of electrode pretreatment on chronopotentiometry and current potential double layer capacitance relations. Capacitance-potential curves were obtained at constant potential in sulphuric acid as a function of the concentration of formic acid and their relations were studied during galvanostatic voltage oscillations. The minimum open circuit potentials were obtained as a function of pH in the presence of nitrogen, carbon monoxide and carbon dioxide. This potential is due to the presence of hydrogen on the electrode. The rise of the potential was caused by the adsorption of an unknown, uncharged species on the electrode. Both the hydrogen and uncharged species, which may be carbon monoxide, were formed from the chemical decomposition of formic acid.

10. **Anode passivation of zinc with a current of alternating polarity**—

L. K. Yuldasheva and F. F. Faizullin (Materially Elektrokhim. Konf., Kazan, Sb. 65, 1959). Anode passivation of zinc in alkaline solutions takes place in two stages. The first stage occurs at a negative potential of the order of -1.1 to 1.2 V. The duration depends on concentration and temperature of the alkaline solution and becomes longer with the increase in temperature and concentration. Thus anode dissolution takes place. But as the concentration of zincate reaches a maximum, the electrode become passive due to partial coating of the electrode surface with zinc hydroxide or zinc oxide. In the second stage an oxide film is formed on the surface. In the case of prolonged anode polarization accompanied by generation of oxygen, the oxide film showed a good crystalline structure corresponding to zinc oxide.

11. **Anodization phenomena on aluminium and aluminium alloys**—

M. J. Brabers (Corrosion Reactor Mater., Proc. Conf. Salzburg, Austria **1**, 369, 1962). In the study of anodization aluminium and aluminium alloys from ammonium nitrate and diammonium hydrogen phosphate the rapid peaking of the potential-time indicated the occurrence of sudden chemical reaction at certain potential values during anodization. The reaction appeared to depend on a metal/oxide interface reaction during passivation. A break occurred in the surface film, exposing free aluminium metal to the oxidizing environment. Number of active sites and time peaks are increased by coarser polishing agents.

12. **Kinetics of the anodic oxidation of tantalum in 30 per cent sulphuric acid**—

V. O. Lavrenko (Zh. Fiz. Khin., 37, No. 10,

2376, 1963). Anodic charging curves and polarization curves were recorded for crystalline and cold rolled specimens of tantalum in 30% sulphuric acid. The energy of activation for a proposed intermediate rated determining step in the electrode reaction which involved the oxidaion of tantalum and oxygen molecule ion was low. The lower oxides and tantalum pentoxide we suggested to form in the anode film.

13. **The reduction mechanism of permanganic ion in mineral acid media**—

Piergiorgio Desideri (J. Electroanal. Chem., 6, No. 5, 344, 1963). A study of the reduction of permanganic ion in nitric, perchloric and sulphuric acids on a bubbling platinum electrode and the influence of acid anions, and the role of di and trivalent manganese on the reduction process, was made. Evidences have shown the formation of trivalent manganeacid complex in sulphuric and perchloric acid. The reduction of the surface film manganese oxide (Mn_2O_3) on the electrode was studied.

14. **Galvanostatic investigation of the cathodic process of hydrogen evolution of cobalt and nickel in acid sulphate electrolytes**—

V. I. Kravtsov, I. O. Maslyakova, and Zh. Gombozhav (Zh. Fiz. Khim., 37, No. 10, 2333, 1963). The investigations carried on the cathodic evolution of hydrogen on cobalt and nickel cathodes, prepared by depositing the respective metal on a platinum wire, in normal magnesium sulphate, at a pH 3-5, have revealed that evolution of hydrogen from water molecule took place when hydrogen ions in the electrode layer were discharged. The concentration polarization is controlled by slow diffusion. The product it $\frac{1}{2}$ (where i is current density, t_{tr} is transition time) is independent of current denisty.

15. **Hydrogen absorption of α-titanium alloys by cathodic polarization**—

N. D. Tomashov, er al. (Korroziya Metal i Splavov, Sb, 167, 1963). The study of kinetics of cathodic hydrogenation of titanium, titanium with a high oxygen content and titanium alloy with 4.35 per cent aluminium in a mixture of 0.03N sulphuric acid and 0.5N sodium sulphate, have shown that quantity of hydrogen absorbed at constant current density is proportional to square root of time. All the hydrogen absorbed by titanium during cathodic polarization is located in the hydride layer which grows due to the low hydrogen solubility and low diffusion coefficient. The controlling factor in the range of current density 20-80 ma./sq. cm., is the diffusion of atomic hydrogen inside the hydride and metal. If aluminium or oxygen is present then the hydrogen absorption of titanium decreases.

16. **Influence of current-density on hydrogen absorption and corrosion of titanium alloys**—

N. D. Tomashov, V. N. Modestova, and A. S. Anatol'eva (Korroziya Metal i. Splavov, Sb. 176, 1963). The thickness of the hydride layer attains a value of 20 microns and remains constant even at higher current densities. The hydride layer growth during the cathodic polarization of titanium in 3N sulphuric acid follows the rule of parabolic square. Titanium alloy containing 4.35 per cent aluminium in 3N sulphuric acid, as the current density is increased first forms a hydride layer passes through a maximum thickness and decreases. But at low current densities the potential is changed into the negative side thus generating a protective effect which disappears as the current density is increased.

17. **Principles of corrosion in liquid metals under isothermal polythermal conditions**—

V. I. Nikitin (Zh. Prikl. Khim. 36, No 10. 2192, 1936). The isothermal as well as polythermal corrosion depends on the rate of solution constant α, and saturation concentration n_∞ although the weight loss in polythermal is independent of time whereas the weight loss in isothermal corrosion increases with time to a constant maximum. Under isothermal conditions, $R_{iso} = \alpha\rho\eta_{(\infty)} \exp(-\alpha St/V)$ where Riso is the rate of corrosion, p is the density of the liquid metal medium, V is the volume of the bath, S is the surface of the specimen and t is the duration of exposure. α is replaced by $\alpha_0 + \epsilon v$ underdynamic conditions with aliquid moving at a velocity V.

18. **A thermodynamic criterion for the inhibition of iron with chromate**—

T. Markovic and Z. Palvolovic (Werkstoffe u. Korrosion **14**, No. 11, 947, 1963). Inhibition by chromate is explained on the basis of affinities of the chemical coupling reaction of anodic iron electrode and the cathodic chromium electrode reactions. The pH dependent inhibiting action of chromate is demonstrated by a

diagram of free energy versus cell potential and pH.

19. Electrochemical behaviour of iron in hydrochloric solutions—

W. J. Lorenz, H. Yamaoka, and H. Fischer (Ber. Bunsenges. Physik. Chem., **67**, No. 9, 932, 1963). The anodic current density-potential curves for the systems iron in hydrochloric acid and in a mixture hydrochloric acid and potassium chloride, show an agreement with Henssler's explanation of iron solution but the anodic Tafel lines indicate that the mechanism of iron solution is affected by specific adsorption of chloride ion.

20. The electrochemistry of the dissolution of zirconium in aqueous solutions of hydrofluoric acid—

R. E. Meyer (J. Electrochem. Soc., **111**, No. 2, 147, 1964). Capacities, steady state polarization curves and galvanostatic polarization curves were obtained during the dissolution of crystal bar zirconium in aqueous solutions of hydrofluoric and sulphuric acid, and the data were explained by assuming that the dissolution reaction involves the continuous formation and dissolution of a film on the surface of the metal which is controlled by the rate of mass transfer of undissociated hydrofluoric acid to the surface of the film.

21. Ethyl alcohol oxidation at platinum electrodes—

R. A. Rightmire, et al. (J. Electrochem. Soc., **111**, No. 2, 242, 1964). The capacitance measurements obtained during the oxidation of ethyl alcohol on platinum, can be interpreted as indicating that ethyl alcohol adsorbs on platinum electrodes in normal sulphuric acid as $MeCH(OH)_2$ in the voltage range +0.3 to 1.0 v. and as $MeCH_2O$ in the voltage range from 0.9 to 1.4 v. At 1.2 v. platinum forms a irreversibility adsorbed oxide film which is not catalytically active but becomes highly active on reduction of this oxide. Acetaldehyde behaves similarly.

22. Mechanism of crevice corrosion—

I. L. Rozenfel'd and I. K. Marshakov (Corrosion **20**, No. 4, 115t, 1964). A special apparatus, where crevice width can be adjusted, and electrochemical methods were used to find out the causes of crevice corrosion. Iron, aluminium and stainless steels were exposed to a mixture of salts and acids. Much destruction of the metals in crevices is due to the acceleration of anodic reaction and decelaration of the cathodic reaction. The potential difference between the metal on the open surface and that in the crevices initiate corrosion cells. This type of mechanism is observed in case of linear selective dissolution of iron in acids, and in water-line zone corrosion.

23. The effect of temperature on the kinetics of nickel-ion discharge—

A. T. Vagranyan, M. A. Zhamagorstyan and L. A. Uvarov (Iza. Akad. Nauk SSSR, Ser. Khim. 1964(2), 301). The calculation of activation energy, W, for the reduction of nickel ion in normal nickel sulphate, from ln i versus 1/T plots, has shown that the process is of diffusion controlled. Polarization at lower temperatures is due to the adsorption of impurities which exhibits inhibiting action.

24. Kinetics for electrooxidation with the simultaneous evolution of oxygen and for electroreduction with the evolution of hydrogen—

N. E. Khomutov (Zh. Fiz. Khim., 38, No. 2, 514, 1964). The equations, relating the current yield to the duration of the electrolysis, concentration of the starting material, temperature, nature of the electrodes and electrode potential, have been derived which can be used to evaluate the effect of various factors on the rate of the reaction and also to determine the reaction mechanism.

25. Theory of electrodissolution of films from the surface of an indifferent electrode—

Kh. Z. Brainina (Dokl. Akad. Nauk SSSR, **154**, No. 3, 668, 1964). The theoretical interpretations for the formation and dissolution of films of difficulty soluble electrolytic products lead to the derivation of formulas for the density of the electrodissolution current, and the potential at which the current attains its maximum value. Experimental values for the system $2Tl^+ + 6OH^- / Tl_2O_3.nH_2O + 2e$, agree well with the equations derived.

26. Passivation of iridium in hydrochloric acid solutions—

J. Llopis and L. Jorge (Electrochim. Acta, **9**, No. 1, 103, 1964). Anodic corrosion of iridium in solutions of hydrochloric acid proceeds through the formation of $IrCl_6^{2-}$ and $IrCl_6^{3-}$; the formation of latter tends t be more important at less positive potenitals. Iridium passivates easily by adsorbed oxygen. At lower

concentrations of hydrochloric acid iridium passivates even for the lower current densities. At concentrations higher than 4N polarization curves show two parts; the first corresponds to anodic dissolution of the metal and the second to evolution of chlorine and oxygen on the passivated metal. The surface oxidation decreases as the concentration of hydrochloric acid.

27. **The behaviour of the copper electrode in alkaline solutions upon alternate anodic and cathodic polarization—**

A. M. Shams El Din and F. M. Abd El Wahab (Electrochim. Acta, **9**, No. 1, 113, 1964). The behaviour of copper electrode upon repeated anodic oxidation and cathodic reduction is studied and found that copper oxidizes to cuprous oxide and cupric hydroxide in the first anodic half cycle and more to cupric oxide (Cu_2O_3) at advanced cycles which is resulted from the oxidation of $HCuO^-_2$ ion. The passivation of copper follow the relation $i\tau^{\frac{1}{2}} \approx 80(OH^-)$, i being the current and the time elapsing until oxygen evolution starts. The reduction of cuprous oxide, cupric hydroxide occurring at more negative potentials than their formation values is due to the semi-conducting properties of these oxides.

28. **Macrokinetics of processes on porous electrodes—**

O. S. Ksenzhek (J. Electrochim Acta, **9**, No. 5, 629, 1964). A general discussion of the kinetics of reactions at porous electrodes is given on the basis of the thermo-dynamics of irreversible processes. The mechanism of the action of gas-diffusion electrodes in fuel cells is discussed. The degree of porosity and the size of the pores is considered in relation to the electrode efficiency.

29. **Studies on the electrochemical mechanism of reduction of carbonyl compounds—**

J. P. Stradins (Electrochim. Acta, **9**, No. 6, 711, 1964). Polarographic studies of cyclic β-diketones and heterocyclic carbonyl compounds lead to establish the role played by protonized complexes, the intermediate free radicals or radical anions, in the electrode process, as well as to follow the change in the mechanism of the electrode reaction occurring with a change in the character of the reaction medium. The values of half wave potentials were compared with those calculated from theoretical equations. The experimental data can be used to interpret chemical reactivity of the compounds.

30. **On the crystal orientation of electrodeposited metals—**

N. A. Pangarov (J. Electrochim. Acta, **9**, No. 6, 721, 1964). Calculations were made for the formation of work, Whkl' of the two dimensional nuclei of metals with cubic, hexagonal and tetragonal lattices. It is shown that the orientation of the crystals of electrodeposited metals depends upon the overvoltage during deposition and it is also suggested that the preferred orientation depends upon the work Whkl. Experimental results for copper, iron, nickel, cobalt and tin deposits agree with theoretical treatment. The influence of the basis metal upon the orientation is discussed.

31. **The anodic passivation of gold and copper in hydrochloric acid—**

G. Just and R. Landsberg (Electrochim. Acta, **9**, No. 6, 817, 1964; in German). The galvanostatic and potentiostatic studies of anodic passivation of gold and copper in hydrochloric acid have revealed that the passivation time in the case of gold is determined by transport process, whereas in the case of copper formation of primary coverages plays an essential part. The theoretical relationship between current density and passivation time is derived for the case of stationary pre-polarization.

32. **Open circuit reduction of chemisorbed oxygen on platinum—**

A. Hoffman and A. T. Kuhn (Electrochim. Acta, **9**, No. 6, 835, 1964). The open circuit reduction of chemisorbed oxygen on platinum electrode in presence of a dissolved depolarizer, such as formic acid, is shown to proceed by a purely electrochemical mechanism. It is unnecessary to invoke an initial chemical reduction. The concept of such a reduction is not supported by the measured rate of reaction.

33. **The electrochemical behaviour of electrodeposited β-cobalt in aqueous acid solutions in presence of iodide ion—**

S. Rashkov, K. L. Hampartzumian and N. A. Pangrov (Electrochim. Acta, **9**, No. 6, 841, 1964). The influence of iodide upon the dissolution of β-cobalt electrodes and hydrogen evolution in normal sulphuric acid solutions was investigated. Iodide ion greatly increases the hydrogen overvoltage and decreases the rate of anodic dissolution of the cobalt electrode. It is suggested that iodide ions are adsorbed on the active places of the cobalt electrode, thus decreasing the dissolution rate.

34. **Adsorption effect of the participants in the electrode and preelectrode reactions upon the kinetics of eletrochemical processes—**

S. G. Mairanovskii (Electro-chim. Acta, 9, No. 6, 1964). The equations were derived for waves of processes with the adsorption of participants in the chemical reactions preceding the electrochemical step proper. If the rate of the surface chemical reaction is great enough the wave height reaches the diffusion limiting current. The peculiarities of the quasi diffusion waves which are common in polarography of organic compounds, the reduction of which involves proton consumption at the potential determining step, are also considered.

35. **Some characteristics of oxidation reactions of organic compounds on platinum electrodes—**

V. S. Bagotzky and Yu. B. Vasilyew (Electrochim. Acta 9, No. 7, 868, 1964). The characteristic shape of the polarization curves obtained during the anodic oxidation of various organic compounds, and the kinetic inhibition of the oxidation process have been shown to result from the change in the electrode state due to oxygen adsorption. The order of the reaction is fractional at moderate concentrations and zero order at higher concentrations.

36. **On the anodic passivity of tin in alkaline solutions—**

A. M. Shams El Din and F. M. Abd El Wahab (Electrochim. Acta, 9, No. 7, 883, 1964). The anodic oxidation of tin was studied in sodium hydroxide solution of different concentrations. The primary passivity is due to the film of stannous hydroxide or tin oxide. Permanent passivity sets in when stannic hydroxide is formed. In concentrated alkali solutions larger quantities of electricity are charged to the electrode to compensate for the chemical dissolution of hydroxides. Interruption of the polarizing current at the oxygen-evolution potential gives rise to a pH-independent arrest which is ascribed to the chemical dissolution of metastannic acid. The anodic behaviour of tin electrode in solutions containing stannite and stannate is similar to that in solutions devoid of these ions.

37. **On the cathodic reduction of manganese dioxide in alkaline electrolyte—**

G. S. Bell and R. Huber (J. Electrochem. Soc., **111**, No. 1, 1, 1964). The equilibrium potentials of several varieties of manganese dioxide at various stages of reduction have been measured and an interpretation offered in terms of the phase changes involved. An explanation of the lattice collapse observed in gamma-manganese dioxide has been suggested.

38. **Effect of velocity and oxygen on corrosion of iron in sulphuric acid—**

Z. A. Foroulis and H. H. Uhlig (J. Electrochem. Soc., **111**, No. 1, 13. 1964). In deaerated acid, low carbon iron corroded at the same rate under either stagnant or high-velocity conditions. In aerated stagnant acid, the rate was lower than in deaerated acid and increased markedly with velocity. In case of carbon steels the rate decreased to a minimum and then increased linearly with velocity. These results can be explained as that presence of small amounts of oxygen increase anodic polarization by adsorption on anodic sites, whereas large amounts of oxygen cause cathode de-polarization, increasing corrosion. The velocity is without effect in the absence of oxygen or the reaction is controlled by activation polarization.

39. **Ionic mass transfer in flowing solutions. Electrochemical reactions under ionic mass-transfer rate control on cylindrical electrodes**

J. C. Bazan and A. J. Arvia (Electrochim Acta, 9, No. 5, 667, 1964). The electro-deposition of copper and the oxidation-reduction reactions for the ferro-ferri cyanide systems were examined. The influences of concentration, rate of flowing, viscosity and diffusivity, height of the working electrode, temperature and distance between anode and cathode were studied under stream line-flow conditions. The heats of activation for copper ion deposition, ferricyanide reduction and ferrocyanide oxidation were obtained. A departure from reverisibility was observed for the oxidation-reduction system reaction when suitable experimental conditions are chosen. This was due to the fact that the kinetic constant increases when the flow rate is increased and also when the electrode height is decreased.

40. **An electrochemical study of thin adsorbed oxygen films on rhodium in oxygen-saturated acid solution—**

J. P. Hoare (J. Electrochem. Soc., **111**, No. 2, 232, 1964). The rest potential of rhodium electrodes in oxygen-saturated acid solutions was determined as a function of time, pH partial pressure of oxygen, and history of

electrode preparation. The Rh/Rh-O system consists of an adsorbed layer of oxygen atoms on the rhodium surface, and the Rh/Rh_2O_3 consists of an adsorbed layer of rhodium trioxide (Rh_2O_3). These oxide films are quite different which may be traced to two different types of bonding between the rhodium and oxygen atoms.

41. **The mechanism of electrolytic rectification**

A. Middlehoek (J. Electrochem. Soc., **111**, No. 3, 379, 1964). A proton current mechanism has proposed to explain the phenomena of electrolytic rectification. When the valve metal is negatively polarized, protons from the electrolyte can diffuse through the oxide film under the influence of applied field. The protons arriving at the metal/metal oxide interface will be neutralized to hydrogen atoms which can either dissolve interstitially in the metal or collect at the interface.

42. **Kinetics of redox reactions on passive electrodes—**

A. C. Makrides (J. Electrochem. Soc., **111**, No. 4, 392, 1964). Overpotential measurements were done for ferric ferrous couple on passive nickel, iron and titanium. Tafel lines were obtained. A limiting anodic current was observed on iron and titanium under certain conditions. In general the passive film has rectifying properties in addition to usual Faradaic rectification observed. The results demonstrate the existence of a potential drop across the passive film, the magnitude of which depends on the thickness and composition of the film.

43. **Kinetics of ferric-ferrous reaction on iron-chromium alloys—**

A. C. Makrides (J. Electrochem. Soc., **111**, No. 4, 400, 1964). The results of the study of electrode knietics of the ferric-ferrous couple on passive iron-chromium alloys have shown that an appreciable fraction of the total potential drop on anodic polarization occurs within the passive film which is associated with changes in the average oxidation state of cations between the inner and outer layers of the surface oxide. A change in the kinetes of ferrous oxidation in the transpassive region of the alloy is due to the production of ferric or hexavalent chromium ions in the inner oxide layer.

44. **A study of surface oxides on platinum electrodes—**

J. S. Mayell and S. H. Langer (J. Electrochem. Soc., **111**, No. 4, 438, 1964). Surface oxides on smooth platinum, electrodeposited platinum black, and platinum black-polytetrofluoroethylene molded electrodes have been characterised by anodic oxidation and cathodic stripping. The oxidation sequence for smooth platinum and platinum black electrodes is $Pt \rightarrow Pt(OH)_2 \rightarrow Pt(O)_2$. At higher potentials smooth platinum forms $Pt(O)_4$ and PtO while platinum black forms $Pt(O)_{2.5}$. The failure of platinum black to form tight PtO may be due to irregular platinum atom arrangement and related to its catalytic properties.

45. **The kinetics of anodic oxidation of iron in neutral solution I. Steady growth region—**

N. Sato and M. Cohen (J. Electrochem. Soc., **111**, No. 5, 512, 1964). During the anodic oxidation of iron, the rate of film growth could be expressed by an equation. A model is proposed based on a 'place-exchange" mechanism in which all the metal-oxygen exchanges in a given row take place simultaneously. This mechanism would lead to an increase of activation energy with thickness and a probable change of mechanism at some finite thickness.

II. **Initial stages—**

N. Sato and M. Cohen (ibid., 519, 1964). When passive iron is oxidized galvanostatically a potential arrest is observed in the initial region. Polarization curves lead to an equation of the form $i = \propto' \exp(\beta' E)$. It has shown that the ratio of iron in the outer layer of the film to charge passed is considerably smaller in the initial region than in the following steady growth region. In the initial region the charge passed was used in the formation of iron-ion vacancy-electron pairs and the transfer of oxygen from the solution to the outer layer of the oxide. The extent of this depends on the thickness of the film.

46. **The passivity of zinc in aqueous solutions of sodium carbonate and sodium bicarbonate**

H. Kaesche (Electro-chem. Acta, 9, No. 4, 383, 1964). In molar sodium carbonate solution passivation is fast and brought about by small amounts of oxide. The current efficiency with respect to oxide formation prior to passivation is high. In 0.1M and 0.01M sodium bicarbonate solutions the passivation is slow and the amount of oxide necessary for passivation depends on the temperature. The current efficiency of oxide formation here is small due to parallel dissolution of zinc to zinc ions.

47. **Investigation of the electric double layer in salt metals—**

E. A. Ukshe et al. (Electrochim. Acta, 9, No. 4, 431, 1964). The capacitance/potential curves for number of liquid metals have a minimum at the potential of zero charge of the metal. Quantitative correspondence between the capacitance curves and the electrocapillary curves has been established. The behaviour of lithium and sodium halides differs markedly from that of potassium and caesium halides. The possible structure of double layer in salt melts is discussed.

48. **Influence of adsorption of neutral molecules and organic cations on the kinetics of electrode processes—**

A. N. Frumkin (Electrochim. Acta, 9, No. 4, 465, 1964). The influence of descending branches on the I/E curves in the case of some electroreduction and catalytic hydrogen evolution reactions can be explained by assuming that the rate is proportional to the amount of reacting particles adsorbed. At coverages approaching unity, increase in the coverage may lead to a reduction in the reaction rate. The orientations and adsorption energies of adsorbed molecules may vary from one metal to the other.

49. **Electrode kinetics on the fluorine evolution—**

Nobuatsu Watanabe, Mamoru Inoue and Shiro Yoshizawa (J. Electrochem. Soc., Japan, 31, No. 4, 168, 1963). The mechanism of the fluorine evolution in the fused KF-2HF electrolysis was discussed from the analysis of the Tafel's equation and the oscillogram. The minimum anode potential is different from the standard potential since the solvation energies with water and hydrofluoric acid are different. Due to differences between the crystal structures of platinum and carbon, the overpotential on platinum was lower. The discharge reaction of the fluoride ions on the anode carbon attached with the fluorine atoms was the rate determining step.

50. **Influence of pH on corrosion and passivation of nickel—**

D. E. Davies and W. Barker (Corrosion, 20, No. 2, 47t, 1964. Anodic and cathodic polarizations of nickel were studied. It has been shown that passivation is caused by the formation of a monomolecular layer of $Ni(OH)_2$ in alkaline solutions and by 1-2 molecular layers in borate solution. On further oxidation, the hydroxide becomes oxidized to Ni, O_2 and finally to a non-stoichiometric oxide (NiO1.8) which is unstable and decomposes when the electrode is made cathodic. The current density has a critical effect on polarization characteristics.

51. **Mechanism of electrochemical corrosion of metals under insulating coatings I Kinetics of deterioration of insulating coatings on metals in electrolytes—**

(Corrosion, 20, No. 4, 125t, 1964). Mechanisms involved in the destruction of insulating films on metal surfaces in electrolytes were investigated. Loss of corrosion-protective properties of the film was found to be due primarily to penetration of the electrolyte, through film pores and defects, onto the metallic surface. The electrochemical nature of the metal and magnitude of its corrosion potential in the particular electrolyte are other important factors in the initial deterioration for the insulating film.

52. **Changes in the activity of the cathode surface in the simultaneous discharge of hydrogen and zinc ions—**

A. F. Nikoforov (Zh. Prikl. Khim., 37, No. 3, 348, 1964). The simultaneous discharge of hydrogen ions and zinc ions from solutions containing zinc, hydrochloric acid and small amounts of cobalt, nickel or copper, was studied. The partial polarization curve of hydrogen passed through a deep minimum. This was ascribed to the cementation of the zinc surface by the impurities. The exchange current of hydrogen on such surface was higher than on pure zinc. The hydrogen overpotential on pure zinc was higher than on cobalt. The overpotential versus log current curve for zinc coated with cobalt lies between the plots for pure zinc and pure cobalt.

53. **The mechanism of the electrochemical oxidation of oxalic acid—**

J. W. Johnson, H. Wroblow and J. O'M. Bockris (Electrochim. Acta., 9, No. 5, 639, 1964). Oxalic acid oxidation on platinized platinum was studied in sulphuric acid, sodium sulphate and sodium hydroxide solutions. Reaction rates were measured. Coulombic efficiency of oxidation to carbon dioxide is 100 per cent. No oxidation in alkaline solutions. The mechanism proposed is that the undissociated acid is the reacting species, oxidation occurs under Temkin conditions, both electrons are supplied by the organic species, and second charge transfer is the rate determining step.

54. **Mechanism of anodic reactions during electrolysis of sulphates**—

A. I. Brodskii, et al (Khim. Perekisnykh Soedin, Nauk SSSR, Inst. Obshch Neorgan. Khim, **18**, 1963). When sulphates and sulphuric acid were electrolysed with platinum electrodes, the electrochemical reactions of formation of peroxydisulphate oxygen and ozone were parallel and independent. The higher platinum oxides are formed from water hydrogenperoxide and peroxymonosulphuric acid and take part in the formation of oxygen and ozone.

55. **The electrolytic oxidation of simple aldehydes and alcohols at platinum electrodes**—

C. Liang and T. C. Franklin (Electrochim. Acta, **9**, No. 5, 517, 1964). The electrolytic oxidation of methyl, ethly and propyl alcohols, formaldehyde and formic acid was studied. The reaction is first order with respect to the organic compound and to the area of the electrode. The platinum hydroxide formed at the electrode oxidize the organic compounds.

56. **Oxygen and hydrogen peroxide electrochemical behaviour on gold electrodes**—

G. Bianchi, F. Mazza, and T. Mussini (U.S. Dept. Com. Office Tech. Serv., AD 276, 134, 16 pp., 1961). Polarization curves in acid, neutral and alkaline solutions were drawn for oxygen and hydrogen peroxide reduction processes and for hydrogen peroxide oxidation process. The current yields for the cathodic reduction of oxygen and hydrogen peroxide were determined in acid solutions.

57. **The effect of soils on the mechanism of copper deposition**—

H. B. Linford and Leonard Karasyk (Tech. Proc. Am. Electroplaters' Soc., **59**, 19, 1963). Stearic acid soils reduced the transfer co-efficient in over-potential studies, indicating that a diffusion process rather than charge transfer was the rate determining step.

58. **Hydrogen overvoltages on electrodeposited beta-cobalt**—

N. A. Pangarov, S. Rashkov and K. Hampartzumian (Electrochim. Acta, **9**, No. 5, 569, 1964). The change of hydrogen overpotential with time was studied. An approximate equation is proposed using which rate constant of combination can be calculated on assuming that slow combination of the adsorbed hydrogen atoms is determining factor of overpotential. Activation energy can also be calculated. The adsorption of iodide ion shows the rate of combination.

59. **Relation between electronic structure and polarographic behaviour of inorganic depolarizers. VII. Determination of activation energy of electrode processes**—

A. A. Vleek (Collection Czech. Chem. Commun., **24**, No. 11, 3538, 1959). A method for determining the real activation energy and frequency factor of the electrode process is based on the temperature dependence of the polarographic wave. The use of derived equations is shown in examples of oxidation of V^{3+}, reduction of $CO(NH_3)_6^{3+}$ and reduction of $Cr(NH_3)_6Br^{2+}$.

60. **Polarographic currents showing simultaneous influence of steric effect and the change in ψ-potential in the presence of surface active ions**—

J. Kuta and J. Weber (Electrochim. Acta, **9**, No. 5, 541, 1964). The electrode process can be accelerated by the adsorption of ions. An inhibition can occur due to the large size of the molecules. This steric effect is observed with nonpolar surface active substances. Formulas for the instantaneous and mean currents are derived. Very good agreement of the shape of the current/time curve with that calculated theoretically is found. The shape of the curves is calculated for cases where the electrode reaction is accelerated by stearic and electric effects, and finally inhibited or accelerated by the change in ψ-potential only.

—(Miss) M.S.