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Ethereal Electrolytes for Aluminium Plating

A.Levinskas

The review deals in detail with ethereal electrolytes widely used at the present time for the formation of high-quality aluminium coatings and mandrels at room temperature. The most important postulates of the theory of electrode processes in ethereal media are discussed on the basis of the latest classification of ethereal electrolytes. The industrial applications of electrolytic aluminium-plating processes and prospects for their further development are briefly enumerated. The bibliography includes 106 references.

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I. INTRODUCTION

Aluminium electroplating yields coatings and electroforming mandrels having a wide variety of physicomechanical properties and at the same time capable of meeting the complex requirements demanded of such coatings by modern instrument engineering, electrical engineering, radio electronics, space technology, and optics. The applications of ethereal electrolytes operated at room temperature are the most promising. In the last decade they have been used in a number of technological processes and industrial technological developments. The experience gained in the employment of ethereal electrolytes enriched the electroplating technology by fundamentally new procedures for electrodeposition in hermetically sealed electrolysers. Furthermore the group of ethereal electrolytes for aluminium platings is the object of current electrochemical studies. Numerous data on the compositions and chemical, electrolytic, and physicochemical properties of ethereal electrolytes and on the characteristic features of electrocrystallisation involving non-aqueous media have now accumulated. All these data refer, in Bockris's terminology[1], to the ionics and electronics of non-aqueous solutions and liquid phases, i.e. important branches of modern electrochemistry.

The review deals systematically with all the known ethereal electrolytes for aluminium plating and describes the most important results of their electrochemical study.

II. ETHEREAL AMINE AND ETHEREAL HYDRIDE ELECTROLYTES

One of the early studies on ethereal electrolytes for aluminium plating was the development of the ethereal amine baths by Doumas and Murphy[2,3]. The general composition of ethereal amine electrolytes may be characterised by the following proportions of the initial components used to prepare the electrolyte: anhydrous aluminium chloride (on average 10–45 mole %), an alkylamine including up to three alkyl groups and up to twelve carbon atoms in the molecule (20–40 mole %), and an aliphatic ether incorporating up to six carbon atoms (30–80 mole %). The electrolytes are prepared by adding, with stirring, the ethereal aluminium halide solution to the cooled amine diluted with the ether. According to the authors, refined electrolytic aluminium is deposited over a wide range of cathodic current densities (up to 0.130–0.140 A cm^{-2} inclusive), but preliminary treatment with a current is necessary. The working temperature of the ethereal amine baths is mainly 20–30°C. The gas used to produce the hermetic seal is dry nitrogen or argon. Best results were obtained for electrolysis in electrolytes prepared using the following components: n-butylamine, ethylhexylamine, and diethyl, dipropyl, and butyl ethyl ether or tetrahydrofuran.

Brenner frequently noted the unsatisfactory reproducibility of the composition of ethereal amine electrolyte. Menzies and Salt[4] subsequently showed that the reproducibility is fully ensured only when chemically pure components and anodes of specially pure aluminium are employed. The authors improved the technology of the preparation of ethereal amine baths before use and the procedures for their employment, as a result of which high-quality elastic aluminium deposits were obtained with thicknesses up to 1–2 mm with an average current yield of 78–80%. Consequently ethereal amine electrolytes are suitable both for electroplating and galvanoplastics.

The development of an NBS (U.S. National Bureau of Standards) process by Brenner, based on his ethereal hydride bath, has had a considerable influence on the development of research into ethereal electrolytes for aluminium plating[5-9]. The composition of the ethereal hydride electrolyte, expressed in terms of the concentrations of the initial components was as follows: 1–4 M anhydrous aluminium chloride, 0.5–1.0 M lithium hydride or 0.1–0.4 lithium tetrahydroaluminate, and absolute diethyl ether. The electrolyte was made by mixing the components in different ways, but in all cases the optimum conditions for the Wiberg–Schlesinger reaction must be maintained[10].

The ethereal hydride electrolyte has excellent electroplating properties. The aluminium deposit contains only traces of heavy metals. A deposit 20–25μm thick is continuous, cryptocrystalline, and elastic. These qualities as well as the 100% current yield of aluminium are maintained at different rates of electrocrystallisation up to values of the order of 0.10–0.15 A cm^{-2} inclusive.

Galvanoplastic layers up to 2–5 mm thick can also be obtained using the NBS electrolyte. Special electroforming procedures make it possible to vary the actual thickness of the mandrel. The NBS ethereal hydride electrolyte is usually hermetically sealed under dry nitrogen or argon. The exposure of its surface to air during the replacement of the electrode rods must be reduced to a minimum. When the requirements of an effective hermetic seal, regular filtration, adjustment, and periodic replacement of the spent anolyte are observed, continuous operation of the bath around room temperature is possible for 15–18 months. Brenner proposed also other ethereal hydride electrolytes, the components of which are sodium or potassium hydride, fused aluminium bromide, butyl ethyl, dibutyl, and diphenyl ethers, anisole, phenetole, etc.[11] However, cathodic deposits of the highest quality and the highest operating efficiency of the baths were achieved only in the NBS process.

The successful development of the ethereal hydride electrolyte for aluminium plating enabled Brenner to turn subsequently to the study of the possibilities of the preparation of analogous hydride systems. Thus they obtained titanium–aluminium, titanium–zirconium, beryllium–boron, magnesium–zirconium, magnesium–titanium, and magnesium–beryllium alloys from an ethereal hydride–tetrahydroborate electrolyte and beryllium–aluminium and magnesium–aluminium alloys from an ethereal hydride electrolyte[12–14]. Subsequently the method for the preparation of the beryllium–aluminium alloy was improved by Lui and Guidotti[15]. It is noteworthy that all cathodic deposits of the above alloys are formed in the form of a powder or strained coatings. Therefore the method of their electrodeposition is of extremely great theoretical value.

Certain electroplating problems of the NBS process have been examined also in studies by other investigators. A microscope study of the structure and properties of the aluminium deposit as a function of its thickness and the nature of the cathode material was carried out by Elze et al.[16] The changes in the morphology, texture characteristics, and microhardness of the deposits after a prolonged operation of the bath (up to 1200 Ah) were studied with the aid of an electron microscope by Addison et al.[17] The high purity of the aluminium deposit obtained from an ethereal hydride electrolyte was confirmed spectroscopically and by X-ray diffraction in studies of Hayashi and Ishida[18,19], while Takahashi and Nomura improved the conditions for the attainment of optimal electrolysis conditions[20].

The need for the improvement of the operating conditions of ethereal hydride baths led to the creation of the so called modified ethereal hydride electrolytes for aluminium plating. McGraw[21] and subsequently Smith and McGraw[22] proposed an "involatile" hydride electrolyte with an ignition point increased to 85–90°C (the Lovet electrolyte). Compared with the ethereal hydride NBS electrolyte, the Lovet electrolyte contains only a very small proportion of diethyl ether in a free state. The presence of alane complexes in the Lovet concentrate requires very careful protection of the latter from atmospheric carbon dioxide. A disadvantage of the Lovet electrolyte is a somewhat reduced conductivity $(0.7–0.8) \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$, so that an increased potential is needed. Subsequently special ionising additives were selected and synthesised. The most effective is 2-ethoxyethyltrimethylammonium chloride, the addition of which to the Lovet electrolyte increases its conductivity to $(0.1–0.2) \times 10^{-1}\ \Omega^{-1}\ \text{cm}^{-1}$. A variant of the modified Lovet hydride electrolyte (the Etmac electrolyte) with an enhanced conductivity was proposed by McGraw and improved by Beach and coworkers[23,24]. The aluminium deposit obtained in the Etmac electrolyte is less elastic and its microhardness is almost twice as high as the average microhardness of electrolytic aluminium.

A group of modified ethereal hydride electrolytes with a more complex composition was developed by Japanese investigators—Ishibashi, Hanamura, Yoshio, Kurata, and others[25–32]. The composition of the electrolytes was based on the optimum ratio of the volume fractions of the ether (tetrahydrofuran or its derivatives—2,3-dichlorotetrahydrofuran, 3-chloro-2-methyltetrahydrofuran, 3-bromotetrahydrofuran, 2-methyltetrahydrofuran, and 2,2-dimethyltetrahydrofuran) and the hydrocarbon (benzene, chlorobenzene, toluene, xylene, dichlorobenzene, and chlorotoluene). For example, in one of the variants the set of components of the modified electrolyte contained 58 vol.% of tetrahydrofuran, 42 vol.% of the hydrocarbon, 0.7–1.0 M aluminium chloride, and 0.2–0.7 M lithium tetrahydroaluminate. The cathodic current density was 0.01–0.05 A cm^{-2}, the experiments were performed at room temperature, the thickness of the coating was up to 0.1 mm, and the purity of the deposit was 99.999 wt.%. The role of the hydrocarbon additive consists in increasing the conductivity. Diethyl, dipropyl, diisopropyl, or dibutyl ethers can be used as other additives and poly(vinyl chloride) or 1,2-dichloroethane can be used as brightening agents. Bright coatings can be obtained in some cases by anodising in the same electrolyte.

The above studies dealt mainly with the solution of problems concerning the composition, preparation, stability, and efficiency of the ethereal electrolytes, the optimal conditions for electrolysis and the principles governing the formation of hermetic seals and adjustment of the baths were established, and the physicomechanical and morphological properties of the aluminium deposits were investigated. Systematic studies on the theory and kinetics of the electrode processes were not made, apart from several investigations on specific problems.

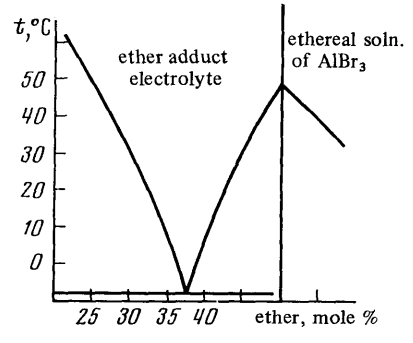


Figure 1. Phase diagram for the aluminium bromide–diethyl ether system.

Connor and Brenner[11] and Clay et al.[33] accumulated extensive factual data on the conductivities of ethereal aluminium halide solutions and an ethereal hydride electrolyte, established the component ratios corresponding to maximum conductivity in the total volume and in the catholyte or anolyte, and investigated the transport of the

hydride component. Using the component ratios thus determined (the ratios of lithium hydride and aluminium halide), the authors put forward suggestions concerning the type of ions promoting the electrocrystallisation of the aluminium deposit. On the basis of a similar correlation between conductivity and composition, Ishibashi and Yoshio[26] attempted to account for the nature of the ionisation of the electrolyte modified with tetrahydrofuran. As mentioned correctly at one time by Kessler et al.,[34] such determinations of the type of ionisation ($Li^+AlH_4^-$, $Li^+AlH_2Cl_2^-$, $Li^+AlHCl_3^-$, etc.) are made without due allowance for the properties of the alane complexes and the nature of the chemical composition and structure of the phases of the ethereal electrolytes.

Individual Tafel relations, obtained in narrow ranges of cathodic current densities, are quoted in reports by Hayashi and Ishida[18,19] and Takahashi and Nomura[20].

III. A NEW CLASSIFICATION OF ETHEREAL ELECTROLYTES

Systematic studies on ethereal electrolytes using a wide variety of electrochemical techniques are being made in our laboratory[35,36]. The objects of the studies are the principal groups of electrolytes: the NBS ethereal hydride electrolyte, the Lovet ethereal hydride electrolyte, ethereal amine electrolytes, and also the etherate, ethereal ammonia, and ethereal dative electrolytes which we proposed. The similarity of their chemical and electrochemical properties is due to the similar proportions of the ingredients in all the groups enumerated.

The etherate of an aluminium halide (chloride or bromide) solvated by the ether constitutes the structural and electrolytical basis of all the phases of the ethereal electrolytes. Diethyl ether is not the only one which can serve, in principle, as the main component of the molecular complex, but it is the most readily available ether, is most convenient to handle, and at the same time ensures the most satisfactory electroplating parameters.

The degrees of solvation of the etherate are various. With an increase in the ether content, a usually slight excess of the so called free ether, which exists in all ethereal electrolytes with the exception of the etherate electrolytes, arises relative to the ether involved in solvation[37].

The next ingredient important for the preparation of ethereal electrolytes (with the exception of those of the etherate type) is a substance (or a set of substances) binding vigorously protons, which are weakly solvated by the ether. This ingredient consists of (a) certain organic bases with high acid dissociation constants, which largely exhibit an n-donor (dative) activity—pyrrolidine, hexamethyleneimine, piperidine, ethylaminocyclohexane, morpholine, N-methylmorpholine, benzimidazole, and indole (ethereal dative electrolytes[38]) and n-butylamine, diethylamine, and triethylamine (ethereal amine electrolytes[39]), (b) ammonia (an ethereal ammonia electrolyte[40]), and (c) the hydride mixture (HM), i.e. the set of products of Wiberg–Schlesinger reaction (alane complexes)[41-48] obtained under the conditions of the preparation of ethereal hydride electrolytes (NBS, Lovet, and Etmac electrolytes[49-53]).

The combination of the above ingredients is important for the attainment of the optimal operating conditions in ethereal electrolytes.

IV. FUNDAMENTALS OF THE THEORY OF ELECTRODE PROCESSES IN AN ETHERATE MEDIUM

Aluminium halide-ether is a 1 : 1 molecular adduct of the highly acidic vacant-orbital acid AlX_3 and diethyl ether as the n-donor: $AlCl_3.(C_2H_5)_2O$.ether and $AlBr_3.(C_2H_5)_2O$. .ether ("ether" is the part of the ether involved in solvation). Compared with other bases, diethyl ether exhibits one of the most intense dative interactions in relation to AlX_3.

The thermochemical characteristics are as follows; the heats of formation of the molecular complexes (in the crystalline state) are ΔH_f(cryst.) = −18.6 ± 0.2 kcal mole^{-1} for $AlCl_3.(C_2H_5)_2O$ and ΔH_f(cryst.) = −23.2 ± 0.2 kcal mole^{-1} for $AlBr_3.(C_2H_5)_2O$; the heat of formation of $AlCl_3.(C_2H_5)_2O$ is ΔH_f = −247.91 ± 0.95 kcal mole^{-1} and the heat of formation of the $AlCl_3$ acceptor itself is ΔH_f = −170.77 ± 0.25 kcal mole^{-1}.[54-58]

The high stability of aluminium halide-ether has been confirmed by studies on the physicochemical phase diagrams for the binary[59] and ternary[60,61] systems and also spectroscopically[62]. Thus the characteristics of the electrode processes in ethereal electrolytes should be determined essentially by the electrolytic properties and the nature of the ionisation of the etherate, while the effect of the remaining ingredients is indirect. According to a thermochemical calculation and infrared spectrophotometric and Raman spectroscopic data for the crystalline state and infrared spectrophotometric and ^1H NMR data for the solutions[34,62-66], the type of ionisation of the etherate (and certain related molecular complexes) is determined by the thermodynamically favourable stable tetrahedral structure of AlX_4^- and the competitive interaction of the Al–O and Al–X bonds (dative bonds):

$$AlI_3 \cdot \text{ether} + AlI_4^- . \qquad (1)$$

Allowance for the dimerisation of aluminium halide in melts and solutions leads to a similar scheme:

$$Al_2I_6 \cdot \text{ether} + Al_2I_7^- . \qquad (2)$$

The etherate electrolytes (the region of melts to the left of the dystectic above the liquidus line on the phase diagram for the aluminium bromide-diethyl ether[67]) is the structurally simplest electrochemical system among ethereal electrolytes. The dystectic (Fig. 1) corresponds to the equimolar composition of the complex $AlBr_3$. $.(C_2H_5)_2O$. The specificity of the composition of etherate electrolytes consists in a complete absence of n-donor additives and free ether; the molecules of the etherate are subject to the ionising action of homopolar aluminium bromide dimers[68,69]. It is noteworthy that the region to the right of the dystectic corresponds to the ethereal solution of aluminium bromide (the etherate in an excess of free ether)–the initial mixture for the preparation of all remaining ethereal electrolytes.

When ionisation of types (1) and (2) occurs in the etherate electrolyte, the stages involving the electrodeposition of aluminium in the presence of Al_2Br_6 as the active acceptor are as follows: reduction of the complex cation with liberation of the unstable Br^- ions and free ether molecules; addition of Br^- to Al_2Br_6 with formation of the particularly stable $AlBr_4^-$ structure; addition of ether to Al_2Br_6; transfer of $AlBr_4^-$ from the cathodic region; transfer of $AlBr_n.\text{ether}^{(2/n)+}$ ions (n = 1 or 2) to the cathode. This results in a redistribution of the substance in the electrolyte (in the presence of a membrane between the catholyte and anolyte)—ether is transferred by the solvated cations to the catholyte. The transfer of

ether decreases the density of the catholyte (the isothermal transition to the left of the dystectic implies an increase in the density of the melts—Fig. 1). The coefficients of the variation of the density of the working electrolyte with time are $\Delta\rho = -0.025$ g cm^{-3} per ampere-hour (catholyte) and $\Delta\rho = 0.021$ g cm^{-3} per ampere-hour (anolyte). The stages involving the addition of the decomposition products of the complex cation to Al_2Br_6, unhindered by steric effects, are more distinctive on increase of temperature and on increase of the content of the free acceptor. Such a change in the conditions governing the reduction of the cation reduces the aluminium overvoltage, which is clearly indicated by the constant-resistance polythermal cathodic polarisation plots (Fig. 2). The decrease in the content of the Al_2Br_6 acceptor should somewhat increase the contribution of the diffusion-dependent rate-limitation of the cathodic process, since the enrichment of the surface layer of the electrode in ether at the instant of the reduction of the cation becomes more distinct under these conditions. The effective activation energy for the cathodic process diminishes correspondingly (Table 1).

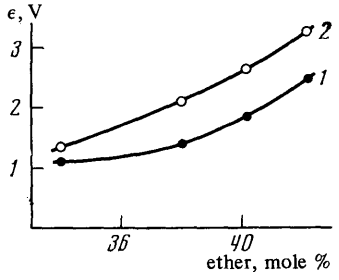


Figure 2. An example of constant-resistance polythermal cathodic polarisation plots for a liquid gallium electrode: 1) electrolyte specific conductance $\kappa = 2.0 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$; 2) electrolyte specific conductance $1.5 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$; $i_C = 0.02$ A cm^{-2}; temperature range 25–50°C.

Table 1. The effective activation energies for the cathodic process (kcal mole^{-1}).

ϵ, V	Ether, mol %				ϵ, V	Ether, mole %			
	41	38	36	32		41	38	36	32
2.00	5.6	7.1	7.8	8.0	2.95	4.8	5.7	6.2	6.9
2.48	5.5	5.8	6.4	7.1	3.43	4.5	5.1	5.3	6.4

The ether molecules arising at the cathode surface interact in a complex manner with the electrolyte. After the enrichment of the electrode surface in ether, the latter adds to Al_2Br_6 or to cations the inner sphere of which may contain several molecules of the base. The interaction with the cations begins to predominate when the concentration of the Al_2Br_6 acceptor in the electrolyte falls. The capture of ether molecules by the inner sphere of the cation increases structural strain. Consequently the reduction of such a cation is facilitated and the rate of the process increases at a constant potential. This conclusion has been confirmed experimentally (Fig.3): the hysteresis polarisation branch as a rule lies above the forward branch, since the cations acquire an additional activity in the region of the reversal of the potential scan. Fig. 3 illustrates the increase of the current by the section *ao* or *cd* ($\Delta i_C > 0$). Δi_C increases with temperature ($\Delta i_C/\Delta t = -0.00023$ A cm^{-2}) and with increase of the Al_2Br_6 concentration in the electrolyte (Table 2).

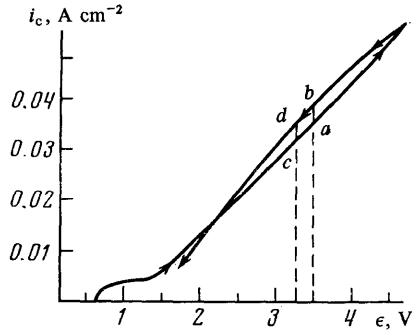


Figure 3. Cathodic polarisation curve for a copper electrode; electrolyte—38 mole % of ether; scan—2.0 V min^{-1}; $t = 20$°C (reference electrode—platinum).

Table 2. The increment of the hysteresis branch Δi_C (A cm^{-2}) ($t = 20$°C; 2V min^{-1} scan; copper electrode).

Compn. of electrolyte, mole % of ether	Δi_C	
	ϵ = 3.25 V	ϵ = 3.50 V
40	0.54	0.47
36	0.47	0.40
31	0.33	0.22

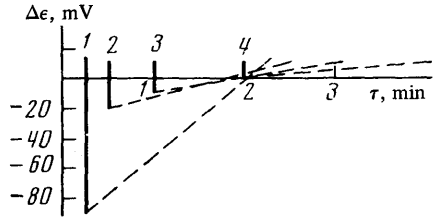


Figure 4. Variation of the probe cell potential after switching off the current pulse: 1) after the first (15 s) pulse; 2) after the second (30 s) pulse; 3) after the third (1 min) pulse; 4) after the fourth (2 min) pulse; continuous lines—variation of Δϵ at the instant of switching off the current pulse; dashed lines—return to the initial potential; copper cathode; $i_C = 0.02$ A cm^{-2}; electrolyte—38 mole % of ether; $t = 20$°C.

The inner sphere of the cation contains together with ether up to two electron-donating Br^- ions, which, having been liberated in the overall electrode reaction and having reacted with the acceptor molecule, stimulate the anodic flux of $AlBr_4^-$ (or $Al_2Br_7^-$) ions. At the instant when the

cathodic current pulse is switched off the increase of the surface $AlBr_4^-$ concentration is manifested by a negative shift of the potential of the platinum probe. In view of the occurrence of the slow reaction between the added free Br_2 and Al_2Br_6, the effect is weaker in subsequent current pulses (Fig. 4).[70,71]

The weak supporting electrolyte in ethereal electrolytes limits the anodic polarisation curve to a single horizontal section located directly beyond the Flade potential (Fig. 5). A passivating film, which is at the same time soluble in the electrolyte is formed along section *bcd*. When this film is observed visually, the anolyte is at the same time seen to be coloured brown. The changes in the electron surface can be compared with the following mechanism for the oxidation of the $AlBr_4^-$ (or $Al_2Br_7^-$) anion:

$$AlBr_4^- - e = AlBr_{3(film)} + \frac{1}{2}Br_2. \qquad (3)$$

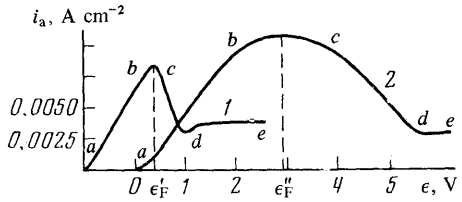


Figure 5. Anodic polarisation curves for aluminium (curve *1*) and platinum (curve *2*) electrodes in an etherate electrolyte.

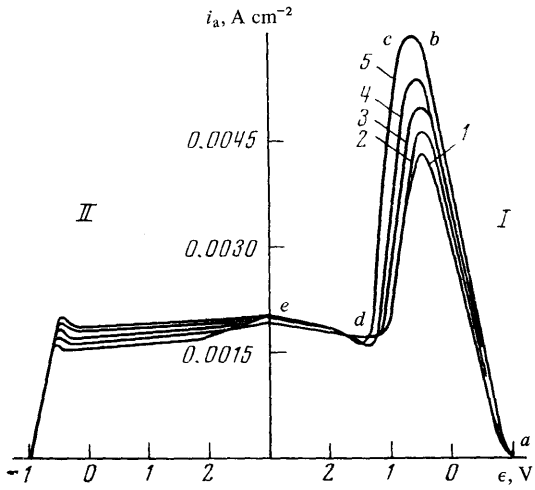


Figure 6. Anodic polarisation curves for an aluminium electrode; electrolyte—31 mole % of ether; scan—2.0 V min^{-1}; t = 25°C: I) forward branch; II) hysteresis branch; rate of rotation of disc electrode (rev. min^{-1}): 1) 400; 2) 800; 3) 1200; 4) 1600; 5) 2000.

Since Br_2 interacts vigorously with aluminium, the colour of the anolyte at the aluminium anode is weaker than at the platinum anode. Owing to the additional Br–Al bonds, the film on the surface of the soluble electrode is more stable, [the passivation maximum is sharper, there are no maxima on the hysteresis branches, and the shape of the polarisation curves changes only slightly when the rate of stirring is altered (Fig. 6)].

Mechanism (3) has been confirmed by studies on the physicochemical properties of the passivating film and on the colour of the surface layer at the anode.

Together with the characteristic absorption wavelength of the Al–O bond (460 nm), the absorption spectrum of the electrolyte (Fig. 7, curve *1*) usually shows a band corresponding to the Br_2–Al_2Br_6 bond (560 nm). The absorption intensity at 560 nm clearly increases following the addition of bromine to the anolyte. A similar increase of the intensity of the absorption band at 560 nm is observed also under the conditions when the electrolyte becomes brown on passivation of the anode (Fig. 7, curve *4*).

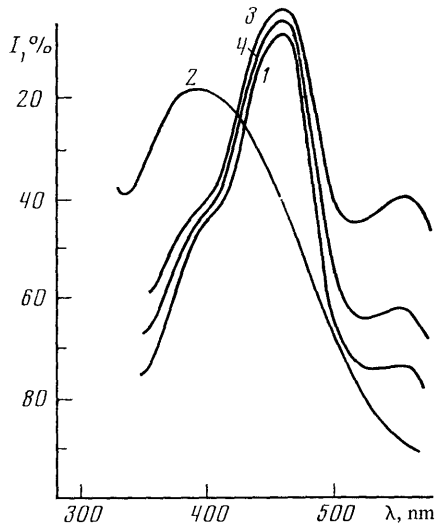


Figure 7. The spectrum of an etherate electrolyte (anolyte): 1) spectrum of electrolyte; 2) spectrum of bromine; 3) spectrum of electrolyte with added bromine; 4) spectrum under the conditions of the brown colour of the electrolyte during the passivation of the anode.

The solubility of the film in ethereal electrolytes of different compositions varies in the same way as the solubility of pure aluminium bromide (Fig. 8). The film dissolves faster in media with a reduced concentration of the free acceptor (Fig. 9). The *bcde* section of the anodic polarisation curve (Figs. 5 and 6) shifts similarly on increase of temperature (0.001–0.004 A cm^{-2} for Δt = 10 degC) or of the rate of stirring. The dissolution of the passivating film in the anolyte (30–32 mole % of ether; volume 30–40 ml) increases its crystallisation temperature on average by 4–5 degC, corresponding to a quantity of electricity of 0.30–0.35 Ah, i.e. displaces the phase equilibrium in the anolyte to the left along the liquidus line (Fig. 1); the same is observed when aluminium bromide is added.

Mechanism (3) for a soluble anode in etherate electrolytes must be supplemented by the indirect dissolution stage

$$\frac{3}{2}Br_2 + Al_{(anode)} = AlBr_{3(film)}. \quad (4)$$

The occurrence of indirect dissolution, which is in general characteristic of the oxidation of anions of the $AlBr_4^-$ type, rules out conditions for the occurrence of disproportionation reactions. At potentials more negative than ϵ_F (Fig. 9) the current yield of the metal in the region of the active electrode surface is almost independent of the rate of stirring (Table 3)[72-74].

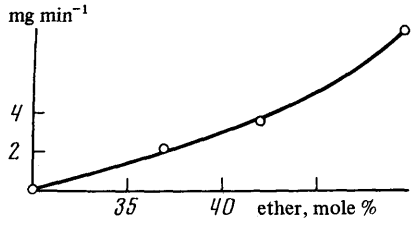


Figure 8. Rate of solution of anhydrous $AlBr_3$ in uniformly stirred etherate electrolytes of different compositions; $t = 50°C$.

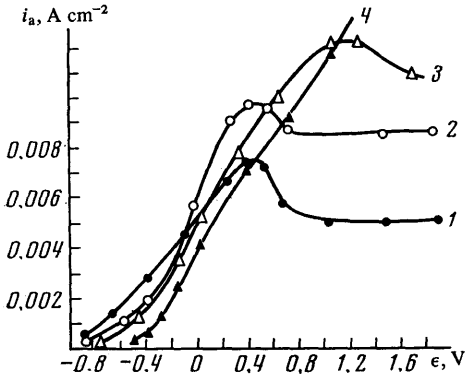


Figure 9. Anodic polarisation curves for an aluminium electrode; amount of ether in electrolyte (mole %): 1) 34; 2) 39; 3) 46; 4) 50.

Table 3. The anodic current yield of aluminium (38 mole % of ether in electrolyte; $i_a = 0.005$ A cm^{-2}; $t = 22°C$).

rev min^{-1}	η_a, %	rev min^{-1}	η_a, %
—	93.5	1000	101.3
600	98.1	1500	106.8

The NBS ethereal hydride electrolyte is structurally most complex among other ethereal electrolytes, since in this case the aluminium halide-ether medium contains the components of the hydride mixture (HM). The composition of the hydride mixture in the range of the initial molar component ratios usually adopted for the electrolyte, $A = LiH : AlCl_3 = 1.40 : 0.25$, varies within fairly narrow limits. If the set of alane complexes is expressed by the molar ratios of the initial monomers $AlHCl_2$, AlH_2Cl, and $LiAlCl_4$ and account is taken of their interaction with the etherate (the mole of the etherate refers by convention to one mole of the monomer), then the typical proportions of the components of the hydride mixture in the etherate medium are readily obtained on the basis of the results of elemental chemical analysis (Fig. 10). The wavenumbers of the absorption bands in the spectra of the electrolyte (534, 492, and 1900 cm^{-1}) correspond to the vibrations of the Al–O, Al–Cl (in $AlCl_2^-$), and Al–H bonds.

The volume of free ether and the ether involved in solvation in the electrolyte is always limited by the total solvating capacity of the etherate medium. For $A > 1.4$ or on direct decrease of the concentration of the etherate (to less than 1 M in terms of anhydrous aluminium chloride) over the ethereal hydride phase, it is possible for an ethereal layer to appear. The separation into layers occurs also following direct dilution of the electrolyte with the ether. The ethereal layer disappears under the influence of the addition of an ethereal solution of aluminium chloride or under the conditions where $A < 1.4$.

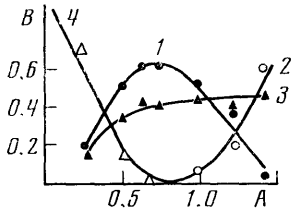


Figure 10. Relative amounts of the components of the hydride mixture in aluminium chloride-ether; A—molar component ratio $LiH : AlCl_3$; mole fraction B (not including the ether): 1) of $AlHCl_2.AlCl_3.(C_2H_5)_2O$.ether; 2) $AlH_2Cl.AlCl_3.(C_2H_5)_2O$.ether; 3) $LiAlCl_4$; 4) $AlCl_3.(C_2H_5)_2O$.ether.

According to the studies of Arkhipov and Mikheeva[47] and Kohler[75], the following mechanism of the ionisation of the hydride mixture is most likely:

$$\begin{aligned} 2AlHCl_2 \cdot AlH_2Cl \cdot ether &\rightarrow Al_2Cl_5 \cdot ether^+ + AlH_4^- \\ Al_2Cl_5 \cdot ether^+ &\rightarrow AlCl_2 \cdot ether^+ + AlCl_3 \cdot ether \\ &\quad \downarrow +AlCl_3 \cdot ether \\ &\quad AlCl_2 \cdot ether^+ + AlCl_4^-. \end{aligned} \quad (5)$$

Anions of the AlH_4^- type are oxidised at insoluble anodes[76] and there is no direct involvement of the hydride mixture in the cathodic process. The potentials corresponding to the deposition of aluminium in ethereal hydride electrolytes and in an ethereal solution of aluminium chloride differ on average by 1–1.5 V, but, on smooth increase (decrease) of the hydride mixture concentration, the limiting current densities with respect to hydride ions are not observed at all (Fig. 11), regardless of the nature of the cathode. The electrodeposition is accompanied by the simultaneous liberation of hydrogen, which has no direct bearing on the current yield of aluminium, the latter being always 100%. This side effect can be accounted for by the

spontaneous decomposition (which is in general slight) of the alane complexes arising under the catalytic influence of the freshly formed surface of the aluminium deposit [78-80].

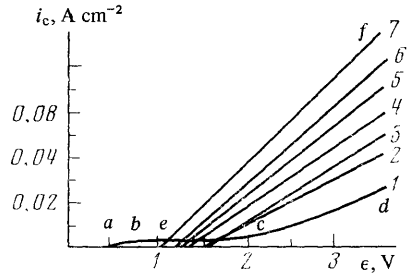


Figure 11. Variation of the cathodic polarisation of an aluminium electrode with increasing content of the hydride mixture in an etherate medium (2 M aluminium chloride, initial volume of electrolyte 30 ml); volume of added hydride mixture (ml): 1) 0; 2) 1; 3) 3; 4) 6; 5) 9; 6) 12; 7) 15; scan—0.8 V min^{-1}; reference electrode—Al(Ag). [77]

The nature of the complex cations of the etherate responsible for the electrodeposition of aluminium and ionisation mechanisms of types (1) and (2) for ethereal hydride electrolytes are to some extent confirmed also by the characteristics of the transport process (electrolyser with a glass membrane, aluminium anode).

Table 4. The transport of ether in the Lovet ethereal hydride electrolyte (i_c = 0.02 A cm^{-2}; volume of electrolyte 50 ml).

t, °C	V_{free}, ml*		V_{int}		Al deposit on cathode		N
	cathode (Cu)	anode (Al)	ml	mole	g	g-atom	
70	3.8	2.2	1.6	0.01533	0.1788	0.00666	2.3
80	3.7	2.7	1.0	0.00958	0.1126	0.00417	2.3
80	4.2	3.0	1.2	0.01150	0.1350	0.00500	2.3

* V_{free} is the volume of free ether collected from the electrode surface and V_{int} is the volume from the inner sphere of the cations.

When an anolyte with labelled chlorine ($H^{36}Cl$) and a non-radioactive catholyte are used at the beginning of electrolysis, the subsequent distribution of radioactivity in the working ethereal hydride bath makes it possible to establish the relation between the diffusion and migration of ions. The migration of $AlCl_4^{*-}$ to the anolyte under the influence of the current in the absence of the Cl^- ligand in the complex cation [81] should in all cases inhibit the diffusional equalisation of the radioactivities of the catholyte and anolyte over a period of time. On the other hand, in the presence of the Cl^- ligand, the effect of the current is varied. According to the Hittorf calculation, in a medium with an equal or greater mobility of $AlCl_4^-$ relative to that of the cation the transport of Cl^{*-} anions to the catholyte is inhibited by migration and for a higher mobility of $AlCl_2.ether^+$ the transport of Cl^{*-} (and hence the equalisation of the radioactivities in the course of time) is accelerated. The acceleration of the equalisation of radioactivities by current in the NBS ethereal hydride electrolyte is observed when the molar ratio A is reduced to values of the order of 0.1–0.2 (Fig. 12). There is apparently an appreciable simultaneous increase in the mobility of the $Al_2.ether^+$ cation.

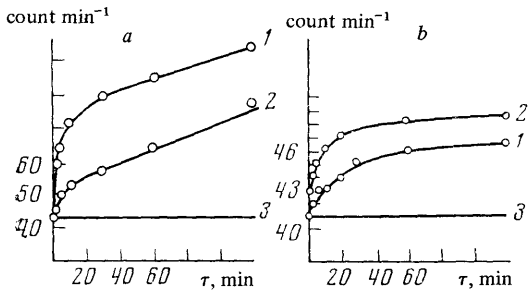


Figure 12. Increase of the radioactivity of the catholyte: *a*) A = LiH : $AlCl_3$ = 0.8; *b*) A = 0.2; 1) diffusion through a membrane (in the absence of a current); 2) superposition of migration (electrolysis); 3) supporting electrolyte; I = 40 mA; electrolyte volume 50 ml.

It follows from mechanisms (1) and (2) that the cation of the etherate is more solvated than the anion with a blocked aluminium atom. Furthermore, at the instant of the reduction of the cation the ether passes from the inner sphere to the free state. The distillation and trapping (by liquid nitrogen traps) of the ether at the instant of the reduction of the cations and the oxidation of the anions of the etherate on the electrode surface are most effective in the Lovet ethereal hydride electrolyte.

The absence of free ether in the Lovet electrolyte makes it possible to determine clearly the difference between the volumes of the ether trapped from the cathode and anode (Table 4). Since the current yield of aluminium at the cathode is 100% regardless of i_c, the ratio of this difference (in moles) to the number of gram-atoms of the aluminium deposit N expresses the number of ether molecules entering into the inner sphere of the cation as the second ligand. The value obtained N = 2.3 is somewhat too high owing to the impossibility of allowing exactly and separately for the total number of ether molecules constituting the solvation shells of the cation and anion, but, according to the results of a study of the transport process, the most probable composition of the cation is undoubtedly $AlCl_2.2(C_2H_5)_2O^+$. The result of the calculation agrees fully with the thermochemical and structural characteristics of aluminium chloride-ether.

In the remaining ethereal electrolytes (ethereal amine [39], ethereal ammonia [40], and ethereal dative [38] electrolytes) the ingredient which binds the solvated protons exhibits a marked chemical individuality. Such ingredients are either organic bases (in ethereal amine and ethereal dative electrolytes; their approximate composition is 1–3 M aluminium chloride or bromide, 5–20 mole% of the base relative to the etherate, and diethyl ether) or ammonia (in the ethereal ammonia electrolyte with the

composition 1–4 M aluminium chloride, 17–30 mole % of ammonia, and diethyl ether) which vigorously bind the protons of the ionised Wiberg-Brown complex[82–84] H. .ether$^+$.AlX_4^-—the product of the interaction of hydrogen halide with the complex cation of aluminium halide–ether. The reaction reduces to the formation of the stable AlX_4^- structure and protons weakly solvated by ether. Therefore the Wiberg-Brown complex is always present in preparations of an ethereal solution of aluminium chloride or bromide.

The distribution of the organic base (and ammonia) in the ethereal electrolyte as a whole is regulated by the equilibria

$$H.ether^+ + base = H.base^+ + ether, \quad (6)$$

$$AlX_3.ether + base = AlX_3.base + ether. \quad (7)$$

In view of the considerable excess of free ether, the low solubility of the type AlX_3.base complexes in the ethereal medium (according to analytical and spectrophotometric data and the results of studies of the electrolytic properties of the systems under consideration), equilibrium (7) is to a large extent displaced to the left[85–88]. Consequently the base is bound by the ethereal aluminium halide solution mainly as a result of the rightward shift of equilibrium (6). This is indicated by the distinct decrease of i_{lim} for the H.ether$^+$ ions (Fig. 13) following the addition of the base. The converging series of values of i_{lim} reflects the existence of equilibrium (6) and its rightward shift.

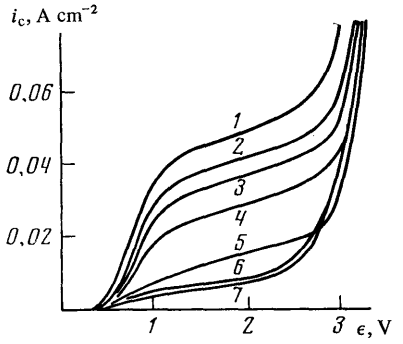


Figure 13. Effect of added base in an ethereal solution of aluminium chloride on i_{lim} for the solvated protons H.ether$^+$; amount of base (hexamethyleneimine, mole %): 1) 0.00; 2) 0.25; 3) 1.00; 4) 1.60; 5) 2.40; 6) 4.00; 7) 6.10.

The Lewis acidity in relation to protons in the bulk of the ethereal electrolyte and in the diffusion layer of the cathode under the conditions of a current can be expressed by the residual concentration of the free H.ether$^+$ ions. The optimum conditions for the electrocrystallisation of aluminium arise only in the absence or at a vanishingly low concentration of the H.ether$^+$ ions, i.e. for a high Lewis basicity of the medium. Otherwise the process is complicated by the presence of the electroorganic component, catalysed by the solvated H.ether$^+$ protons in the presence of free ether molecules (a dark dispersed powder is deposited on the cathode). Etherate electrolytes in which there is no free ether at all constitute an exception. Therefore in etherate electrolytes H.ether$^+$ ions do not exhibit a catalytic activity and a high quality crystalline aluminium deposit is obtained in the presence of even large concentrations of the Wiberg–Brown complexes[89]. A high basicity is always readily generated in ethereal hydride electrolytes owing to the decomposition of the Wiberg–Brown complex by the compounds constituting the hydride mixture [a complete rightward shift of equilibrium (6)][51,79].

The remaining electrolytes [with an incomplete rightward shift of equilibrium (6)] are distinguished by a more complex mechanism for the attainment of a high Lewis basicity. A high quality deposit arises on the cathode only after a preliminary passage of a current (4.0–4.8 Ah per litre of solution), i.e. after an additional decrease of the residual concentration of the H.ether$^+$ ions owing to the electrolytic liberation of hydrogen. In consequence of the low rate of interaction of the complex H.base$^+$ and ether, a steady-state distribution of the components of equilibrium (6), close to the distribution which obtains when the equilibrium is completely displaced to the right, arises under the influence of the current.

When a current is passed through ethereal electrolytes, there are a number of features which reflect directly the changes in electrocrystallisation conditions. The values of i_{lim} for H.ether$^+$ ions on the cathodic polarisation curves fall to zero only as a result of the current (Fig. 14); curve 4 in the same Figure reflects the variation of i with ϵ under the optimal electrodeposition conditions.

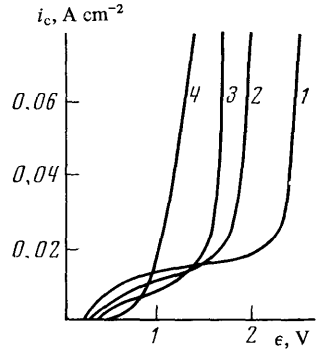


Figure 14. Variation of cathodic polarisation during the passage of a current through the ethereal electrolyte (base—hexamethyleneimine): 1)–3) decrease of the residual concentration of H.ether$^+$ ions (dispersed deposit); 4) electrodeposition under the conditions of high basicity (dense crystalline deposit); galvanostatic conditions; reference electrode—Al(Ag).

The increase of basicity on passage of a current can be expressed quantitatively as an increase of conductivity (Fig. 15) or as a negative shift of the platinum probe potential reversible with respect to H.ether$^+$. The considerable decrease in conductivity can be explained by the weakness of the H$^+$–ether bond ($pK_a = -3.59$) relative to the H$^+$–base bond ($pK_a = 7.3–12.3$)[38]. The reversibility of the probe electrode potential relative to H.ether$^+$ is a result of the saturation of the electrolyte by cathodic hydrogen.

In the presence of Lewis bases and ammonia, potentials of the probe cell in the range between −0.3 and −0.6 V (the probe potential is negative) correspond to optimal electrocrystallisation (a dense crystalline deposit). In the absence of bases (a dispersed deposit is formed regardless of the amount of electricity passed through the system) the potential is limited to 0.0–0.2 V (the probe potential is positive). In ethereal hydride electrolytes the very presence of the hydride mixture alters the cell potential to between −0.9 and −1.1 V, as a result of which the necessity for exposure to a current is eliminated.

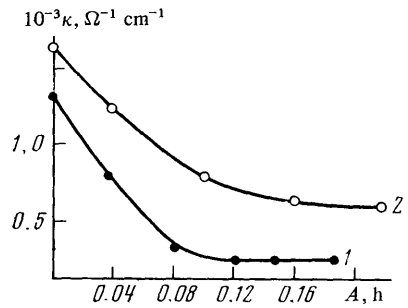


Figure 15. Variation of the conductivity of the ethereal electrolyte during the passage of a current: 1) base—piperidine; 2) base—hexamethyleneimine.

The elimination of the electroorganic component of the electrodeposition process (transition from a dispersed deposit to a dense crystalline deposit) in general increases the purity of the coating. However, under optimal electrocrystallisation conditions in ethereal ammonia and ethereal dative electrolytes, side processes persist at elevated current densities ($i_C > 0.005$–0.010 A cm^{-2}): there is a weak evolution of hydrogen owing to equilibrium (6) and possibly an additional electroorganic reaction. For this reason, in the given group of electrolytes the current yield of aluminium in certain cases does not exceed 75–80% following an increase of i_C and the morphology of the deposit may be complicated by local spheroidal formations[90–92].

The significant characteristics of electrode polarisation in ethereal electrolytes are high exchange current densities [$(2.0–5.0) \times 10^{-4}$ A cm^{-2} in etherate electrolytes and 1.6×10^{-3}–4.3×10^{-4} A cm^{-2} in ethereal hydride electrolytes] and high temperature coefficients of the overvoltage (which usually exceed by an order of magnitude the analogous values in an aqueous medium) 0.01–0.03 V deg^{-1}, as a result of which the kinetics of the reduction of the etherate cations when $i_C < 0.01$ A cm^{-2} depend on the superposition of limitations due to the reaction (in etherate electrolytes), crystallisation, and diffusion (in the NBS ethereal hydride electrolyte; in this case the Faraday impedance can be represented by the equivalent circuits for the transition, diffusion, and crystallisation–see Fig. 16). In the range $i_C = 0.10$–0.40 A cm^{-2} diffusion-dependent limitations fully predominate (ethereal hydride and ethereal ammonia electrolytes). Since free dilution of the etherate phase by ether is ruled out, the properties of the limiting current density of the diffusion overvoltage (the dependence of i_{lim} on the molarity of the etherate, the content of the hydride mixture and organic bases, temperature, rate of stirring, etc.) can be investigated exclusively by a pulse technique. The transition time for strong current pulses can be determined only when a rigorous correspondence between the true and induced currents i_C is maintained (< 0.40 A cm^{-2}). For this purpose, the treatment of the test electrode must ensure the homogeneity of the surface and inhibition of the growth of crystal nuclei during the pulse (galvanostatic switching on)[51,71,80,90,93].

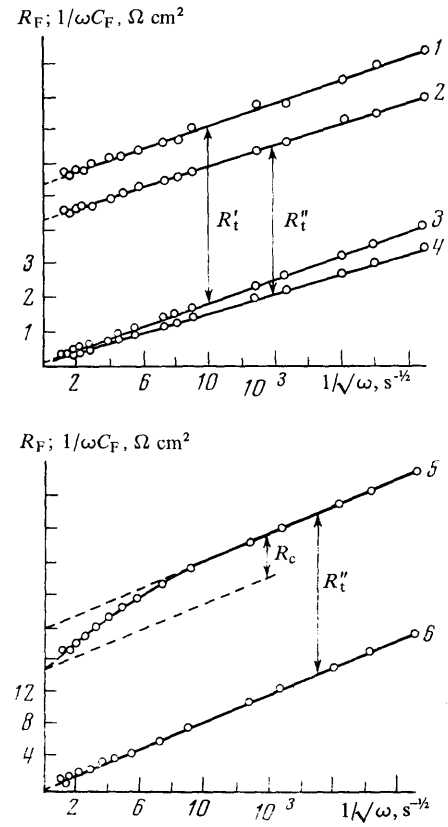


Figure 16. Components of the Faraday impedance; aluminium electrode: 1) R_F; 3) $1/\omega C_F$; Al(Hg) electrode: 2) R_F; 4) $1/\omega C_F$; Al(Hg) electrode: 5) R_F; 6) $1/\omega C_F$; measurements in aluminium bromide–ether.

V. THE OVERVOLTAGE OF HYDRIDE HYDROGEN

The behaviour of soluble and insoluble anodes in all ethereal electrolytes is determined by the oxidation of the AlX_4^- anions from the etherate with the exception of hydride media where the anodic process is complicated by the involvement of the AlH_4^- ($Al_2H_7^-$) ions[75,76,80,81]. In the case of an insoluble electrode AlH_4^- ions are oxidised under conditions corresponding to the first section of the anodic polarisation curve ($i_C \leq 0.01$ A cm^{-2}, $\epsilon \leq 1.5$ V). Consequently the above ranges of the i_C and ϵ values are convenient for the measurement of the overvoltage of hydride hydrogen.

The concept of electrolytic desorption proposed by Heyrovsky is justified by the nature of the protons $H.aq^+$ solvated by water. Hence the hypothesis that the potentials of the spent and anodically polarised electrode in the ethereal hydride electrolyte depend on the Volmer–Tafel mechanism is quite natural. After replacing $H.aq^+$ by $H.hydr.^-$, the mechanism becomes

$$\begin{aligned} H^- &\rightleftharpoons H + e, \\ H + H &= H_2. \end{aligned} \qquad (8)$$

Thus examination of the hydride hydrogen overvoltage could also permit the solution of the problem of the relation between the successive discharge and recombination stages. Calculation of the overvoltage from the Tafel relations or the equations of the Kheifets pulse technique leads to large numerical values of the exchange current density (Table 5) and the coefficient b and to extremely small transition coefficients α (Table 6).

Table 5. The exchange current densities at the hydride hydrogen overvoltage ($-\lg i_0^*$).

Electrode	Temperature, °C				Electrode	Temperature, °C			
	10–12	15–18	24–25	30		10–12	15–18	24–25	30
Ag	3.4	3.2	2.9	2.8	Sn	—	3.6	2.8	2.5
Ni	—	6.0	5.8	5.7	Pb	5.0	4.5	—	3.2
Zn	—	4.5	3.5	3.2	Pt	5.5	5.3	5.0	4.7

Table 6. The coefficients b and α for hydride hydrogen (t = 20°C).

Electrode	b, V	α	Electrode	b, V	α	Electrode	b, V	α
Ag	0.56	0.105	Zn	0.28	0.210	Pb	0.22	0.267
Ni	0.55	0.107	Sn	0.39	0.150	Pt	0.38	0.155

Table 7. A series of Tafel coefficients a at the hydride hydrogen overvoltage.

Electrode	a, V	Electrode	a, V	Electrode	a, V
Pb	0.9	Sn	1.3	Pt	2.0
Zn	1.1	Ag	1.7	Ni	3.4

In terms of the values of b, the Tafel relations for hydride hydrogen express the overvoltage of the transition, i.e. the kinetics of the oxidation of the AlH_4^- ($Al_2H_7^-$) ions are determined by the discharge reaction and not the recombination reaction. Furthermore, the possible influence of the spontaneous decomposition reactions of the hydride mixture on the oxidation of hydride hydrogen reduces the probability of a mixed mechanism for overvoltage of the type under consideration.

The low values of the coefficient α indicate a high activation energy for the reverse Volmer reaction [Eqn. (8)], which is equivalent to hindrance characteristic of the formation of structures deformed by hydride hydrogen. For the hydride hydrogen overvoltage, the sequence of the activation energies for the forward Volmer reaction differs appreciably from the classical sequence, usually represented by a series of increasing Tafel coefficients a (Table 7)[94,95].

VI. INDUSTRIAL APPLICATIONS OF ETHEREAL ELECTROLYTES

The aluminium deposits coating the surfaces of various metals at room temperature in ethereal electrolytes are obtained in the form of dense, homogeneous plate of high purity[8,11,16,18,26,50]. The usual technical procedures (stirring, adjustment of the position of the rods, regulation of the electrolyte stream, periodic filtration, employment of certain additives) make it possible to vary the thickness of such coatings from several micrometers to 2–3 mm, while ensuring at the same time the necessary uniformity. The advantages of electrolytic aluminium (small weight, high thermal conductivity, electrical conductivity, and reflectivity, effective anticorrosion properties, low melting point, only slight deterioration in the properties of the coated metal under the conditions of heat treatment, and low cost) compared with zinc, tin, cadmium, gold, and titanium–silver coatings have greatly increased interest in the aluminium-plating process in ethereal electrolytes in the field of both modern electroplating technique and in galvanoplastics. Mainly ethereal hydrides (NBS, Lovet, and Etmac) electrolytes have been recommended for electroplating baths in technological and industrial-technological processes.

The most important stages in electroplating processes are the choice of the surface to be coated (usually steel, copper, nickel, Kovar, titanium, and silicon), the search for a technique to be used in the preparation of the surface for aluminium plating giving a reliable adhesion of the coating, and the design of a hermetically sealed bath and electrode rods (in an atmosphere of dry nitrogen or argon). Various workers have often used the so called aliphatic acid treatment of the surface, originally proposed by Schickner[96,97]. Before being immersed in the ethereal hydride bath, the metal surface is uniformly coated by a crystalline layer of aliphatic acid (oleic, linolenic, etc.) or by a layer of salicylic, benzoic, pyrogallic, phenylacetic, or heptafluorobutyric acid[11]. The onset of the aluminium electrodeposition process (the switching on of the working current) is synchronised with the dissolution of the layer of acid in the electrolyte. The aliphatic acid treatment requires expensive reagents and must be performed with exceptional precision. The maximum adhesion of the coatings is achieved by selecting the appropriate acid and the appropriate duration of the individual operations in the treatment in relation to various aluminium-plated metals. An easier and universal method of preparing the surface for aluminium plating involves chemical or anodic etching of iron, steel, Kovar, nickel, and copper in hydrochloric acid[53,75], phosphate, nitric acid, and hydrogen peroxide[98–100] solutions, which prevent saturation with hydrogen.

Industrial-technological aluminium plating of constructional titanium rods (NBS ethereal hydride electrolytes) was achieved by Hess and Betz[101]. Aluminium plating at room temperature is hardly reflected in the mechanical properties of the rods. An appreciable corrosion resistance of the components was achieved. The authors note that different variants of their technology

can be used for the aluminium plating of titanium components of more complex shape, certain parts of laboratory and workshop furniture, and also individual units in microelectronics (including, for example, the local aluminium plating of locating frames).

Electroforming techniques for aluminium have found extensive applications (NBS, Lovet, and Etmac ethereal hydride electrolytes). Buschow and Esola[102] and Schmidt and Hess[103] developed a process and designed a manufacturing set up for the construction of high-quality light aluminium reflectors for the concentration of solar energy (18 and 76 cm in diameter). Aluminium layers are grown at room temperature on nickel and silver templets with mirror-bright surfaces. The improvement in the design of the ethereal hydride bath hermetically sealed under argon and nitrogen is noteworthy; the authors increased the volume of the bath to 700–800 litres. The construction of aluminium reflectors was developed in processes used in the manufacture of telescopic reflectors, non-magnetic optical systems, light and precision mirrors, and optical systems for cosmic space apparatus.

Another trend in the development of techniques for electrolytic aluminium plating using ethereal electrolytes involves the electroforming of layers with fillers. The technique of the preparation of matrix composites (with boron rods, silicon carbide, beryllium, steel, and graphite fibres as fillers), which are light, very hard, and at the same time elastic, to be used in the construction of components of cosmic space apparatus, has been proposed and successfully introduced by Hanson et al.[104] and Withers and Abrams[105]. Electroforming techniques for aluminium have considerable advantages over other methods for the preparation of matrix composites, since electrodeposition in the range of room temperatures hardly influences the properties of the fillers themselves, which makes it possible to increase sharply the set of physicomechanical properties of the composites themselves and at the same time achieve an exceptionally high strength to weight ratio for such composites.

A new stimulus to further improvement of the manufacture of solar batteries arose from the technology of the deposition of aluminium layers (NBS ethereal hydride electrolyte) on the surface of silicon sections proposed by Lui and Yasui[106]. Aluminium terminals simplify the construction and parallel connection of aluminium sections compared with the earlier technology in which a titanium–silver alloy was used.

Manufacturing–technological processes involving the electrodeposition of aluminium from ethereal electrolytes at room temperature have greatly increased practical and theoretical interest in this field of electrochemistry.

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Kapsukas Vilna State
University