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ON THE POSSIBILITIES OF USING TITANIUM AS A SOURCE OF ENERGY IN--ETC(U)
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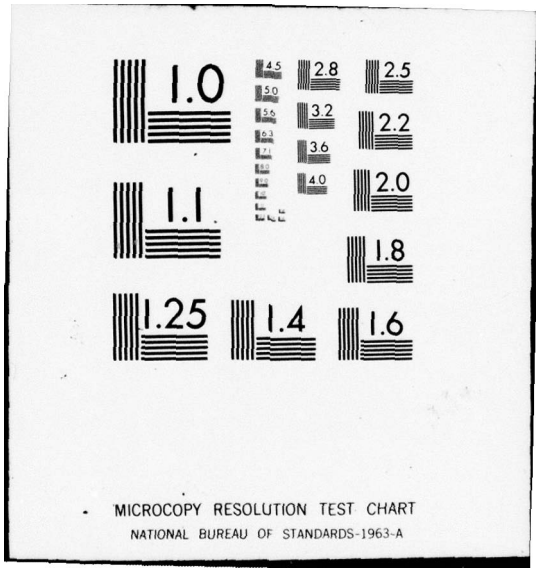
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ON THE POSSIBILITIES OF USING TITANIUM AS A SOURCE OF ENERGY IN RECHARGEABLE BATTERIES

by

M.A. Klochko and E.J. Casey

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RESEARCH AND DEVELOPMENT BRANCH

DEPARTMENT OF NATIONAL DEFENCE
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(6) ON THE POSSIBILITIES OF USING TITANIUM AS A SOURCE OF ENERGY IN RECHARGEABLE BATTERIES

by

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ABSTRACT

Titanium has become available as a commercial metal only after World War II, and, at low price, a decade later. As a recent arrival, Ti has not been utilized as a reactant or energy-supplying material in batteries, despite its advantageous properties -- its low weight-density and the high energy-density of its reaction with oxygen and halogens.

After an introduction on the occurrence and technology of titanium and of the history of its study in the U.S.A. and in the U.S.S.R., its electrochemical behaviour in aqueous, non-aqueous and molten salt media is reviewed. Suggestions on the choice of materials for anodes, cathodes and electrolytes for Ti batteries are presented and several electrochemical reactions on which these batteries are based are discussed.

RÉSUMÉ

Le titane n'est devenu un métal disponible sur le marché que depuis la 2^{e} guerre mondiale et à des prix moyens une dizaine d'années plus tard. Ceci explique le fait que ce métal n'a pas été étudié en profondeur en vue de le rendre susceptible de pouvoir fournir une source d'énergie pour batteries, en dépit de ses propriétés avantageuses, celles de posséder une basse densité et une puissance d'énergie très élevée tant qu'à sa réaction électrochimique avec l'oxygène et les halogènes.

Aprés avoir passé en revue les faits et la technologie du titane, nous présentons les études qui ont été exécutées aux Etats Unis et en URSS, ainsi qu'une discussion sur son comportement électrochimique dans des milieux salins aqueux et non-aqueux et aussi dans des sels fondus. Sont présentées également quelques suggestions sur les choix de matériaux pour anodes, cathodes et électrolytes d'une batterie titane. Nous offrons en plus quelques commentaires concernant différentes réactions électrochimiques sur lesquelles ces batteries sont fondées.

INTRODUCTION

The physical, mechanical and electrochemical properties of titanium which are important in its possible utilization as an active material in rechargeable battery systems have not previously been analyzed, nor have the various relevant papers on the subject been reviewed. Many factors suggest that the time is appropriate to do so.

Titanium is also very abundant in the earth's crust, being the ninth among the elements and the seventh among the metals (see Table I). Ti minerals are not as dispersed as those of lithium, and the metal is more abundant (some 14 times) than the six non-ferrous metals listed in Table I and lithium put together. It is about 33 times more abundant even than zinc, which enjoys great popularity for both primary and secondary batteries.

The price of metallic Ti, $\sim$ \$1.50-2.0 per Kg, is also now not prohibitive, being of the same magnitude as that of Na, Ni or Mg, and three times less than the price of Co or Cd. The growing economic importance of Ti and its compounds is reflected in many reviews, trade publications and diverse uses. The Canadian situation is expressed annually in the Canada Metals Yearbook, for example.

Because of its comparatively low density (4.51g/cm^3) it occupies an intermediate place between the light metals (Na, Mg, Al) and the heavy ones (Fe, Ni, Zn) used in batteries. It holds the same position with respect to energy density: the ED of its oxidation is more than twice as high as that of Zn and four times that of Cu or Cd. Essential electrochemical properties of the metal and certain of its soluble salts indicate promise as negative plate material in some systems and the recently discovered highly conducting intercalation compounds such as TiS_2 indicate promise for the positive plate in others.

However, in spite of all these advantageous properties of Ti, there are not many descriptions in the literature, or even suggestions, of its use in batteries. Even in patents, the use of metallic Ti for batteries is seldom suggested. Such a strange state of affairs can be explained by the early emphasis on preparation of metallic Ti and its technology for the aircraft industry and by the rather special properties of the oxides which form on its surface and which inhibit electrochemical processes and provide good corrosion resistance in all but special electrolytes.

The method is to review critically the relevant published information obtained for other purposes, and to draw the appropriate inferences. The metallurgical, electrochemical and trade literature has been duly searched.

TABLE I

Abundance and Some Other Properties of Metals Suitable for Electrodes in Electrochemical Batteries

Metal	Atomic Number	Atomic Weight	Abundance p.p.m.	Density 20°C	Melting Point °C	Price $/Kg (1971)
Li	3	6.94	65	0.57	180	18.00
Na	11	22.99	28300	0.97	97.5	0.97
Mg	12	24.31	20900	1.74	650	0.80
Al	13	26.98	81300	2.10	660	1.02
Ca	20	40.08	36300	1.53	850	0.76
Ti	22	47.90	4400	4.51	1670	1.36
Fe	26	55.85	50000	7.87	1540	0.55
Ni	28	58.71	80	8.90	1455	2.29
Cu	29	63.54	70	8.96	1083	1.16
Zn	30	65.37	132	7.14	419.5	0.75
Cd	48	112.40	0.2	8.65	321	3.30
Pb	82	207.19	16	11.34	327	0.31

Note: The prices of metals in this Table have only a relative significance, as they fluctuate depending on the degree of purity and many other conditions.

In general the authors conclude that many good possibilities exist for the use of Ti in batteries which deserve experimental examination, and a profitable future is predicted.

DEVELOPMENT OF TITANIUM TECHNOLOGY

Titanium was discovered in the last decade of the 18th century, and although its compounds have been intensively studied since that time, it was obtained in the pure state for the first time only more than one hundred years later, by U.A. Hunter in 1910. It remained a "rare metal", a laboratory curiosity, during the next decades because no acceptable technological method of winning it was discovered. In 1936 W. Kroll disclosed a method of obtaining pure Ti through the reaction of its chloride with molten magnesium according to the reaction:

$$TiCl_4 + 2Mg = Ti + 2MgCl_2. \qquad (1)$$

An article published by Kroll in the Journal of the Electrochemical Society in 1940 [1] is the basis of present technology.

After the end of World War II intensive studies of Ti and its alloys were begun in the U.S.A. and, later on, in other countries. Excellent mechanical and anti-corrosive properties of the metal, and especially of its alloys, were discovered during the first post-war decade. No other structural metal has been studied so intensively and has advanced so rapidly in technological use during a 10-year period. The production of metallic Ti in the U.S.A. increased from 2 tons in 1947 to 15,750 tons in 1957. In 1957 also, 1500 tons of Ti were produced in the U.K. and 6000 tons in Japan. Today several thousand tons are produced manually in the U.S.S.R. Consumption of Ti metal in U.S.A. in 1975 was 17,000 tons.

Titanium and its alloys are used where high strength and low density are important: in aircraft, in armor plates and other military hardware. Due to its corrosion resistance, titanium has found broad applications in various devices of the chemical industry: in pump valves, centrifuges, pipes and electrodes; in foils for hydrofoil boats; in heat exchangers for nuclear systems.

As the technology of winning Ti was perfected, its price dropped, falling from $12.00 in 1959 to $2.53 in 1968 and $1.36 in 1971, per kg of Ti sponge. Refined, Ti is 2-3 times more expensive. High purity material is much more costly, of course.

OCCURRENCE, PRODUCTION AND REFINING. SOME PHYSICAL AND CHEMICAL PROPERTIES OF TITANIUM

Titanium can be found almost in any rock and soil in comparatively small concentrations. There are, however, Ti ores with high content of the metal, in the form of its two main minerals, ilmenite ($FeTiO_2$) and rutile (TiO_2), often associated with magnetite or hematite. Large reserves of Ti ores are found in many countries -- in the U.S.A., the U.S.S.R., India and others.

In Canada a deposit of about 125 million tons of ilmenite, containing about 25-30 million tons of Ti, is situated near Lake Allard, 400 miles north-east of Quebec City. It was discovered in 1948. Quebec Iron and Titanium Ltd. treated over 2 million tons of ilmenite in 1974, and a high grade TiO_2 is now offered, but no metal is produced yet in Canada.

More than a million tons of Ti ores are used annually for the production of titanium pigment TiO_2. The production of TiO_2 is comparatively simple: Ti containing ores (or slags) are leached with concentrated sulfuric acid, and after precipitation of the iron by various agents, the $TiSO_4$ solution is hydrolyzed, dehydrated and dried.

The production of metallic Ti is more complicated. Only a short sketch will be given here of the processes, which are described in detail in the early books of Barksdale [2], Clark [3] and others [4].

Ti ores or slags (the latter being a by-product of pig-iron production from Ti-containing Fe ores) are chlorinated. The $TiCl_4$ so obtained, which is liquid at ambient temperatures, is purified by distillation and introduced into a reactor with molten Mg under an argon atmosphere, where reaction (1) occurs. In England Na is used instead of Mg: $TiCl_4 + 4Na \rightarrow Ti + 4NaCl$.

After the salt is removed, Ti remains in a sponge-like form which is refined, usually electrolytically in a fused-salt bath, or by vacuum-melting. Refining in North America is mostly done in molten NaCl (see Figure 1), but in Europe the lower-melting NaCl-KCl mixture, with or without added $MgCl_2$ is used. Very pure Ti can be obtained by converting the sponge into titanium iodide, followed by the thermal decomposition of the latter.

Of the physical properties of Ti, apart from those cited in Table I, (density and melting point), the existence of two crystal structures should be noted, α and β. Thus at temperatures below 882°C Ti has a hexagonal close-packed structure (the alpha phase), whereas between 882° and its melting

point (1670°C) Ti exists in a body-centred cubic structure (the beta phase). Ti can form various phases with other metals.

According to I.I. Kornilov, titanium enters into solid solutions and compounds with other metallic and non-metallic elements which have metallic, covalent or ionic chemical bonding. The kind of bonding depends principally on the similarity or difference of the atomic radii and the electron structure of the alloying element -- in general, on the position of the element in the periodic system. Thus:

1. The large difference between the atomic radii of the alkali and the alkaline-earth metals on the one hand, and Ti on the other, accounts for the fact that these metals do not interact with Ti, forming neither solid solutions nor compounds. (Beryllium is an exception).

2. Halogens and chalcogens (F, Cl, Br and I; S, Se and Te) form with Ti various kinds of compounds which have covalent or ionic types of chemical bonds. Solid solutions are not formed.

3. The following elements form limited solid solutions with Ti and some intermetallic and covalent compounds also: Mn, Re, Fe, Al, Sn, B, C, N, O and some others.

4. Six metals viz. Zr, Hf, V, Nb, Ta and Mo, form continuous solid solutions with the alpha or beta phases of Ti [5,6].

Details of the phase diagrams of binary systems formed by Ti with other elements can be found in Refs. [7, a, b, c]. Alloys with Al form a class of special importance; the super alphas as well as the $\alpha\beta$ solutions.

The position of Ti in the fourth group of the Periodic System, and the electronic structure of its atom, which places it among the transition metals, define its chemical properties. Since it has 2 electrons in the outer shell and another 2 in the next inner shell outside the 8 which form the stable argon modification, Ti forms stable compounds in which it is tetravalent. It is found in nature in the form of TiO_2. Tetravalent compounds are formed also with the halogens, for instance TiF_4 and $TiCl_4$, which are liquids at ambient temperatures, and $TiBr_4$ and TiI_4, which are solids.

Trivalent compounds are also formed (TiF_3, TiI_3), but the divalent are said to be more stable. The di-and tri-valent compounds are ionized and the tetravalent have covalent bonds. However, there are ionic compounds of the type M_2TiX_6, such as K_2TiCl_6, which are electrochemically active.

Very stable compounds are formed with B, N and C. Titanium carbide is formed at high temperature, so carbon cannot reduce TiO_2 to metallic Ti. Almost all Ti salts are hydrolysed in water [2]. Hydrides of Ti are prominent.

Since the intensity of the reactions between Ti and acid or alkaline solutions depends on the level of purity of the metal, great discrepancies exist amongst the data of various authors who have studied such reactions with Ti containing different amounts of admixtures. On the basis of recent more accurate data it can be concluded that titanium is stable in air, water

and sea brine, but reacts strongly with concentrated HNO_3; it dissolves in HF, hot HCl, and H_2SO_4 and in hot concentrated H_3PO_4. The addition of fluoride ions enhances the dissolution of Ti in any acid.

A large number of organic compounds of titanium have been synthesized and studied during the last decade. However, we have found so far no relevant electrochemical information on these which is appropriate to the present study. The electro-organic aspect of subject needs to be searched more deeply than we have done.

STUDIES OF TITANIUM IN THE U.S.A. AND IN THE U.S.S.R.

The work of the United States Bureau of Mines researchers and other scientists and engineers has transformed titanium from a curiosity into an important structural material. This change, which occurred during the early 1950's, was made possible after the technology of producing Ti on a commercial scale was mastered. However, three main problems connected with the expanded use of Ti in the national economy have appeared since.

1. To improve the technology of Ti production to make the metal less expensive and more readily available.

2. To find the composition of Ti alloys with the most useful technological and structural properties.

3. To study the behaviour of Ti and its alloys under various conditions: high and low temperatures, under the action of various corrosive agents, in acids, alkaline solutions, in molten salts and in hot plasmas.

There is also a fourth problem, which has not yet been formulated precisely: To diversify the use of Ti, to find new fields for its application. One of the possibilities may be the use of Ti in electrochemical batteries, the subject of the present report.

As the advantages of the use of Ti and its alloys in military hardware became clear, the U.S. Department of Defence contracted the Battelle Memorial Institute (Columbus, Ohio) in 1953 for collection, storage and dissemination of information on Ti technology. Many laboratories in the U.S.A., both private and governmental, are occupied in studying Ti. Scores of papers, several books and hundreds of patents have been published in the U.S.A. and Europe [8]. International meetings on the science, technology and application of titanium took place in 1968, 1972 and 1976. Proceedings of the first two Symposia [9a,b] are readily available in English, edited by R.I. Jaffe and H.M. Burke of the Battelle group. The critical review on winning and refining by M. Hoch [9b, Vol. 1, p 205] is relevant. Russian work, not always easily available in English, is reviewed next.

Activity in this field began to develop in the U.S.S.R. from the middle of the 1950's, in scientific institutes, design offices and pilot plants. The investigation of Ti and its alloys -- their structure, physico-chemical and mechanical properties -- is carried out in the Baikov Metallurgical Institute of the U.S.S.R. Academy of Sciences, in Moscow, under the guidance of the Academician N.V. Ageev, Drs. I.I. Kornilov, E.M. Savitsky and others. The corrosion of Ti and its alloys occupied researchers in the Academy's Institute of Physical Chemistry under Dr. N.D. Tomashov. The electrochemistry of Ti in fused salts is studied in the Institute of General and Inorganic Chemistry of the Ukranian Academy of Sciences in Kiev under Drs. Yu.K. Delimarskii and B.F. Markov, and also in the Electrochemical Institute of the Urals Branch of the Academy in Sverdlovsk under Dr. M.V. Smirnov.

Intensive studies on producing and refining Ti in fused salt media have been carried out in the Aluminium-Magnesium Institute (Leningrad) by N.I. Anufrieva, A.I. Ivanov and their co-workers. In the early 1970's a special Titanium Institute was organized from the Titanium Laboratory of the Aluminium-Magnesium Institute. From there, for example, a U.S.S.R. patent, applied for August 28, 1971, claimed protection of a method of passivating Ti and other refractory metal powders by hydrogen absorption. The claim was made by six workers of the All-Union Scientific-Research and Design Institute of Titanium [10].

Many other laboratories of various institutes and universities of the U.S.S.R. are working on Ti as well. Apart from papers on Ti published in the major Soviet chemical journals, like the Journal of Inorganic Chemistry, Journal of Applied Chemistry, Elektrokhimia, Ukranian Chemical Journal, and some technical periodicals, several books on Ti have been published, starting from collections of translations of papers published in foreign periodicals (1953-1954), bibliographical indexes, and continuing with collections of Russian articles in a serial "Titan i Ego Splavy" (Titanium and Its Alloys), which is issued by the Baikov Metallurgical Institute. In the first ten books of this collection issued during 1958-1963 there are papers on metallography, electrochemistry and technology of Ti and its alloys [11].

Although the literature published on Ti world wide is very extensive, it shows only the tip of the U.S.S.R. titanium iceberg. The adopted technology of Ti and the amount of its production in the U.S.S.R. are not published, and the leading personalities of the Ti industry are not widely known through travel abroad. Thus, for example, Dr. S.G. Glazunov, whose report "Titanium in the U.S.S.R." was published in the proceedings of the First International Symposium on Ti, was invited to co-chair the Second Symposium, but he could not. The Chairman of the conference reported later: "Unfortunately Prof. Glazunov was not able to attend. In his place Dr. L. Petrova served ably as head of the Soviet delegation" [9b]. Unfortunately, too, Glazunov's paper "Titanium in the U.S.S.R." is very sketchy.

In his report on the first conference Prof. Glazunov noted that 1950 was the year of the birth of the Ti industry in the U.S.S.R. He listed the metals the alloys of which (with Ti) have been studied in the U.S.S.R., and he demonstrated a short chart of the Ti production there. The process starts with the smelting of ilmenite concentrates to produce pig-iron and Ti slag. The latter, while being clorinated in electric shaft furnaces, produces

$TiCl_4$, which after being refined, is reduced with Mg. The resulting Ti sponge, after being separated from the Mg salt, is melted in an electric-arc furnace. The first Ti sponge was produced in 1954. Without giving the exact figures for Ti production, Prof. Glazunov noted that production tripled between 1961 and 1965 [9a]. The growing interest in Ti in the U.S.S.R. during the 1960's can be illustrated by an interesting observation. The well-known Russian specialist on corrosion, Dr. N.D. Tomashov, published two books on that subject. In the first one, which appeared in 1960 in Russian, (translated into English in 1966) Ti is mentioned only in passing, in a few pages [12]. The second book, published in Russian 5 years later, although it is 3 times smaller than the first one, contains more pages devoted to the corrosion of Ti and its alloys, the amount of the material on Ti in this book being practically equal to that on the most important of construction materials, viz. stainless steel [13]. It is evident that this remarkable surge of interest in Russia parallels the acceleration to world-wide consumption of Ti.

Several conferences on titanium were held in the U.S.S.R. between 1959 and 1970. The Proceedings of the Eighth conference were published in a book issued in 1970 and contain information on heat-resistance of Ti alloys and on corrosion of Ti [14]. It is of interest to note that in an article on Ti published in the "Small Soviet Encyclopedia" in 1960 the usual method of producing Ti consists in reducing $TiCl_4$ by metallic Mg, or in reducing TiO_2 by the hydride of Ca [15], although the latter method apparently has not been developed into production, in the U.S.S.R. or anywhere else.

As will be shown later in this report, it can be inferred that studies of titanium as an active material in batteries may also be in progress in various places in the world, and particularly in the U.S.S.R., although there are very few publications directly on the subject so far.

THE ELECTROCHEMISTRY OF TITANIUM IN AQUEOUS SOLUTIONS

The researcher who intends or wishes to investigate the possibilities of using Ti as a source of power in batteries cannot find much published information directly connected with that topic. One can, however, review these possibilities by studying the abundant material in the literature on the *electrochemistry* of Ti and of its alloys and compounds. This information, although stimulated by the practical needs of the developing Ti industry, provides also some data which are useful for planning purposes, and for suggesting experimental approaches to Ti-containing batteries. Thus, for example, the practical needs of studying the corrosion of Ti in various media -- aqueous, non-aqueous and fused salts -- provide some data on the behaviour of Ti as an anode in those media; and studies of Ti electroplating elucidate its behaviour as a cathode. The large amount of work done and published on the methods of producing and refining Ti in molten salts can be of substantial

help in attempting to design experiments with rechargeable cells. For these reasons the available material on electrochemistry of Ti will be reviewed in this and in the following sections. The present authors have endeavored to study all the available literature from 1947 on which contains some facts or data on the electrochemistry of Ti. Although not pretending to present here an exhausting bibliography on this topic, we hope that the most important works are discussed in this report. Special consideration is given to the abundant Russian literature, some items of which have not yet appeared in English. We will start from the aqueous solutions, having in mind here, as well as in other sections of this report, that the activity, and not the passivity of titanium is of primary interest for the use of this metal in batteries.

ANODIC DISSOLUTION, CORROSION AND POLISHING

The title topics concern the anodic behaviour of Ti. Although most corrosion tests on Ti have been carried out without application of current, the anodic behaviour of Ti in various media is also of interest: thus the imposed current sometimes changes this behaviour but not always. Among many studies of Ti corrosion the work of M.E. Straumanis et al. and that of N.D. Thomashov et al. are selected for discussion. These and other authors have used Ti of different grades of purity (not always indicated in the publication), or alloys the compositions of which are often hidden unspecified within the trade mark. Hence, the results of various workers do not always coincide, and the experiments often cannot be reproduced. As to the huge amount of patent literature on Ti, it is mostly depreciated by the scarcity of data and the vague and generalized descriptions.

Straumanis has carried out experiments with plates containing 99.1% Ti. The metal dissolves very slowly in H_2SO_4 or in HCl below 2N, and still more slowly in HBr at all concentrations. In HI it does not react at all. The protective layer on Ti is easily dissolved in HF and in acids to which a small amount of NH_4F has been added. The potential of Ti in 6N-H_2SO_4 is -0.342V [16]. The anodic and cathodic potentials in acidic and alkaline solutions have been investigated [17].

N.D. Tomashov has measured the rate of Ti corrosion with and without anodic current. The results are exposed in his mentioned above two books, both of which are available in English [12,13]. (See especially the latter one.) In one of his papers Tomashov noted that Ti is one of the most thermodynamically unstable, but one of the most easily passivated, transition metals [18]. Both these properties are of great importance for the use of Ti in batteries. Alloying metals influence the passivity of Ti, increasing or reducing it. The equilibrium potential of Ti against the hydrogen electrode is -1.63V (Ti/Ti^{2+}). The protective film makes its potential more positive [13].

Considerable data on the anodic potential of Ti in various media can be found in the literature. The corrosion potential of Ti in 10M-H_2SO_4

is -580 mV, and in 0.1M H_2SO_4 + 0.9M Na_2SO_4 it is -470 mV [19a]. Several other papers on the anodic behaviour of Ti which can be found in the Journal of Electrochemical Society between 1970-1976, extend earlier published work. The subject continues to intrigue investigators, for example inhibition in strong H_2SO_4 [19b].

Metal-polishing under current may be also considered as an anodic process. Some patents and articles have been published on this topic as well [20].

Stabilization of Ti by Pt, by Pd, or by other precious metal deposits, as Ti-M alloys on the surface, is assuming a large importance in electrolyzers and in electrolytic reactors. The photo-assisted electrolysis of aqueous electrolytes on TiO_2 anodes is being heavily investigated as well. Neither of these phenomena is of importance in the search for battery-active systems, however, and they are not reviewed here. Stress-corrosion-cracking, of paramount importance for other reasons, is of little concern in a proposed battery application, and is not reviewed here either.

The works on Ti corrosion cited above [12-18] and many other publications issued in the 1950's-1960's were called forth by the needs of the construction industry. Therefore the work on corrosion was concerned mostly with atmospheric agents, such as moisture, CO_2, salt spray and the like. However new corrosion agents have become important as Ti and its alloys have found their use in the chemical industry. For that reason the action of acids, halogens, alkalies and so on have become the objects of corrosion studies, and many articles and patents have been published on this topic during the last decade. For example, it was found that F-ions accelerate anodic dissolution of Ti in H_2SO_4 [21]. Further, a patent on corrosion prevention of Ti in various devices was granted in 1973 [22]. Again corrosion and electrochemical behaviour of Ti and its alloys in alkaline solutions was studied in [23] and the effect of hot salt solutions in [24].

ELECTROPLATING OF Ti

N.T. Kudriavtsev, the Russian electroplater whose books are in wide use in the U.S.S.R., has described practical ways to electroplate Ti. His methods include the deposition of Ti from acid and alkaline solutions. The current efficiency always decreases with time, and the quality of the deposit varies widely. Control of the process is difficult, under the best of conditions.

Whereas calculations of the standard potential of Ti places it between Al and Mn in the electrochemical series, experimental data place it between Cd and Co [25].

The difficulties of depositing Ti on the cathode from aqueous solutions are caused, apart from the low overvoltage for the hydrogen evolution reaction, by the capacity of Ti to absorb hydrogen in great amounts,

and by the rapid passivation of Ti in air. The ease of hydrolysis of Ti salts adds a complication. Deposited in a layer of several microns on some metals, Ti forms, in time, solid solutions with them [26]. The role of the overvoltage in Ti deposition is also underlined in Reference [27].

An attempt was made to adopt the electroplating of Ti and its alloys from aqueous $FeCl_2$ solutions for restoration of worn-out machine parts [28].

There are several patents on electroplating and even some on refining Ti from aqueous solutions. However, no evidence has been published up to date on the possibility of obtaining thick Ti layers on the cathodes from these solutions. This problem is discussed in Brenner's monograph on electrodeposition of alloys where the literature up to 1960 is cited [29]. A recent review on electrodeposition of alloys cites the literature from 1960 to 1975. On a diagram indicating binary alloys deposited on the cathode the systems Ti-Ni, Ti-Fe, Ti-Co and Ti-Cd are shown and references on these couples are presented [30].

NON-AQUEOUS SOLUTIONS

The behaviour of Ti anodes in salt solutions in CH_3OH and in its mixtures with water has been studied. NaBr and HCl enhance local dissolution of anodically polarized Ti in CH_3OH. In mixtures of the alcohol with water Ti is anodically dissolved. The potential increases with the increase of water content [31].

The solubility of Ti compounds in various solvents, and also the electrodeposition of the metal has been studied. No metal was deposited from K_2TiF_6 in $Al(BH_4)_3$. However, from solutions of $TiCl_3$ in the $LiBH_4$, a black, moisture-sensitive deposit was obtained [32].

A black Ti powder on the cathode from a 10% $TiCl_4$ solution in iso-BuOH + ethyleneglycol was obtained in a cell with Pt anode and a Hg cathode. However, only 2% of the Ti was extracted from the solution [33].

Metallic Ti can be deposited on the cathode in liquid NH_3 solutions of Ti chlorides. The deposit is often pyrophoric. The decomposition potential varies from 1.3 to 3.4V depending on the kind of salt and its concentration [34].

Ti alloys and Ti hydride behave differently during anodic dissolution in CH_3OH containing 3 mol/l H_2SO_4. The difference in potential, >200 mV, indicates the possibility of separating the hydride from the alloys [35].

ELECTROCHEMICAL BEHAVIOUR OF Ti IN MOLTEN SALT MEDIA

Many relevant papers and patents have been published on the electrochemical behaviour of Ti in fused salts, where the metal is more active than in aqueous and non-aqueous media. Apart from corrosion of Ti, which can even happen in the reactors where Ti is produced at high temperatures, several other processes have attracted the attention of researchers who investigated the electrochemical production and refining and hardening of titanium.

Publications dealing with the electrochemistry of Ti in fused salts can be grouped under three headings: "Potentials and Corrosion"; "Electrolytic Winning of Ti in Fused Salts"; and "Electrolytic Refining of Ti".

POTENTIALS AND CORROSION

Plambeck's recent book [36] gives collated data on potentials of various metals, Ti among them, in several fused salt mixtures. Data on these topics published in Russian have been issued by the two institutes mentioned before in this report, in Kiev by B.F. Markov and co-workers and in Sverdlosk by V.I. Smirnov and his pupils. Most of Markov's works were published in the "Ukranian Chemical Journal" during the 1960's. Examples follow.

The potential of Ti^{3+}/Ti^{2+} in molten KCl-NaCl at 700° is -1.807V, against Cl_2 in molten AgCl [37a]. In NaBr-KBr (1:1 mole) at 700° the potential is -1.553V [37b]. In KI + NaI at 700° against an iodine electrode, the potential of Ti is -0.815V, and in CsI it is -0.907V [37c]. The decomposition potential of a 15% solution of Na_2TiF_6 in NaCl + KCl at 700° is 2.6V [38].

V.I. Smirnov and co-workers have published most of their studies in a special serial, "Proceedings ("Trudy") of the Electrochemical Institute, Urals Branch of the Academy of Sciences". 12 volumes were issued during the 1960's most of which were already available in English under the general title "Electrochemistry of Molten and Solid Electrolytes" (1961-1972).

The electromotive force of cells: $Ti//TiCl_2$ + MeCl//MeCl Cl_2,C has been measured. When Me is Li, the EMF is 2.25V; in KCl it is 2.561V at temperatures above the melting point [39a]. Analogous cells with $MgCl_2$,

$CaCl_2$ and $BaCl_2$ show potentials of 2.279, 2.470 and 2.608V respectively [39b]. In a molten mixture of K, Na and Li carbonates stationary potentials were found: for Ni, -1.210V; Fe, -1.8V; Ti, -0.842V [39c]. Results quoted are typical.

Several articles on corrosion of Ti in fused salt media were published by M.E. Straumanis. In molten NaCl-NaF in the presence of air, Ti is severely attacked at 850°C; the samples disintegrated. Potentials of Ti cells in molten salts were measured [40]. E.K. Kleepies and T.A. Henrie followed the reaction rate of Ti and some alloys in molten chloride melts [9a]. Further, White et al. reported recently on studies done in $MgCl_2$-KCl at 450°C [41], results which indicate continued activity of the metal. Clayton and Mamantov studied active corrosion of Ti in NaCl-$AlCl_3$ [42].

ELECTROLYTIC WINNING OF Ti IN FUSED SALTS

In the flow sheet of Ti production in the U.S.S.R., published in 1961 [43a] and in 1970 [43b], electrolytic winning and refining of the metal are not mentioned. Ti slags from iron production (using ilmenite as the ore), are chlorinated to obtain $TiCl_4$, which, after purification, reacts with Mg to produce Ti sponge. The latter is refined by electric arc melting. However, intensive studies of producing and refining Ti by electrolytic methods are being carried out continuously, and many papers on these topics have been published during the last 15 years: in the Ukranian Chem. Journ., in the Journ. of Applied Chemistry ("Zhurn. Prikladnoi Khimii"), in the serials "Titan i Ego Splavy", in "Electrochem. of Molten and Solid Electrolytes", and in several other Russian periodicals. Some examples are cited below.

Of special interest are the attempts to produce Ti from TiO_2 by electrolysis, similar to the method of winning Al from Al_2O_3. The possibility of Ti production from TiO_2 is claimed, but the conditions are not clarified. The method yields Ti with 1-4% of admixtures. It is less economical than the process with $TiCl_4$ and requires refining. Some details of this process are given in [44].

An attempt has been made to deposit Ti from melts containing TiO_2 in NaCl + K_2TiF_6, with some success at low concentrations of TiO_2, but at high concentrations of TiO_2 the metal is not deposited at all [45].

More successful was an attempt to deposit Ti from an eutectic mixture of 62% K_2TiF_6 + 38% NaCl, to which 2-3% TiO_2 was added at 600-850° [46]. Later, experiments with TiO_2 and rutile were carried out on a larger scale. Impure Ti was obtained, especially from rutile, although the yield was below 60% [47].

Studies on electrochemical production of Ti from $TiCl_4$ and the lower chlorides of the metal have also been carried out in the U.S.S.R. From baths containing molten chlorides of Na, K, Mg, Sr or Ba at 700-750°, in which $TiCl_4$ is dissolved, 90-100% of the $TiCl_4$ is consumed [48]. The solubility of $TiCl_4$ in various melts was investigated -- in NaCl, in an equimolar mixture

of NaCl + KCl [49a], and in $MgCl_2$ [49b]. It is clear, however, that reversible solubility, where the solute preserves its individuality or its ions, does not persist. Reactions occur such as:

$$TiCl_4(g) + 2Cl^- \rightleftharpoons TiCl_6^{2-} \text{ (melt)}.$$

It has been suggested that during electrochemical production of Ti from $TiCl_4$ in molten KCl + NaCl (1:1 by weight), the process passes through two stages. During the first stage $TiCl_4$ is reduced to lower-valency chlorides, which are then electrolyzed to metallic Ti during the second stage [50]. These two stages take place simultaneously, as $TiCl_4$ is reduced to lower chlorides by the electrodeposited Ti. This, and also the reaction between Ti and Cl_2, reduces the yield of the metal to 13-16% [51].

(An inference may be of interest at this point: From some references in the literature it could be supposed that the impetus for the Russian studies of the electrochemical production of Ti was provided by the note published in 1952 by A. Brenner and S. Senderoff in the U.S.A. The authors stated that despite the fact that several laboratories in the U.S. were then working on electrolytic production of Ti powder and plates, no publications on this topic had so far appeared. Publishing their results, the authors invited other workers to do the same [52]. Some 5-6 years after this paper appeared, Russian researchers also started to publish articles on the electrochemistry of Ti, but the experiments must have begun several years earlier. Thus for example, work the results of which were published in 1957 must have required at least two years to be done. These papers, published in the "Transactions of the Al-Mg Institute" (not yet available in Canada), are summarized in the Chemical Abstracts. The articles reflect many and varied experiments on electrolysis of $TiCl_4$ in fused chlorides, done worldwide.)

One very important experimental finding in the work of A.I. Ivanov and V.G. Gopienko was that a deposit containing up to 80% Ti could be produced by electrolysis of $TiCl_4$ in the fused mixture of $AlCl_3$ + NaCl [53a]. Such a system, on account of its low melting point, could be used in batteries containing Ti as one electrode. In another article the same authors give a detailed description of the processes and materials used in the electrolytic production of Ti [53b]. No further work along this line seems to have been published. Confirmation and extension of this work could prove interesting.

The anodic behaviour of TiC and Ti_3N_4, as well as of some Ti alloys, has basic importance in studies of batteries based on Ti. Titanium carbide is thermodynamically very stable, being formed from the elements with a substantial decrease of free energy. Despite this fact it dissolves anodically and behaves like an alloy of two metals under such circumstances. For this reason it has been proposed for the electrolytic extraction of Ti [54]. More than 90% of its Ti content can be extracted in a fused halide bath and deposited on the cathode as a dendritic metal, if the bath is either NaCl + $TiCl_2$ or NaCl + K_2TiF_6.

The behaviour of TiC in H_2SO_4 was studied, to determine the limits beyond which this material cannot be regarded as inert. It is assumed that Ti is converted into an oxide and the C into CO_2 [55].

Nitride-hardening of Ti surfaces can be effected in molten cyanides; the nitride increases resistance to wear [9b, p. 2501]. The anodic behaviour of Ti nitride ($Ti_{1.22-1.27}N$) in fused KCl + NaCl was studied. N_2 is evolved on the anode and Ti^{4+} is introduced into the electrolyte [56].

J.O'M. Brockris has concluded from his experimental work that K_2TiF_6 and $TiCl_2$ can be reduced to Ti only by a secondary reaction with the alkali metal [57]. The same kind of mechanism is proposed by M.E. Sibert to explain the appearance of a Ti deposit on the cathode during the electrolysis of TiO + $CaCl_2$, namely the TiO is reduced by metallic Ca at the anode [58a]. In order that such reactions would not complicate the processes of a storage battery based on Ti, the melt must contain only such cations which cannot be deposited at the cathode under the given conditions or react directly with Ti. However another explanation is given by [58b].

REFINING Ti BY ELECTROLYSIS

This operation suggests the use of Ti sponge, alloy or scrap as the anode, and its deposition as a pure metal on the cathode. As we have seen above, aqueous and non-aqueous solutions are not very appropriate for such a purpose, as no thick and adherent deposits of Ti on the cathode have been so far achieved.

Most of the Ti sponge and flake which is sold commercially in North America today is produced via the Kroll process and refined by molten-salt electrolysis. The anodic and cathodic processes in electrolytic refining are quite similar to the processes of discharge and recharge at the negative plate of a battery, and therefore one can obtain useful suggestions for battery application from studies of electrolytic refining in fused salts. The presence of oxygen or of moisture inside the reactor, the composition of the electrodes (the kind of metal or its admixtures), and the composition of the electrolyte all may provoke side reactions and the contamination of the Ti deposit [59]. These difficulties are seldom mentioned, either by authors of patents (as, for example, in [60]), or even in scientific papers. The papers of Rand and Reimert [61a,b] are an exception: the scheme of the experiments and the influence of the impurities are described clearly.

Background studies of electrolytic refining and of electrochemical production of Ti seem to go hand in hand. In the U.S.S.R. this work is done in the institutes at Kiev and Sverdlovsk, and on a larger scale in the Aluminium-Magnesium Institute in Leningrad, where technical details are worked out on a pilot-plate scale. The former two Institutes concern themselves more with the basic scientific problems. In the Ukranian Institute, for example, Ti sponge was used as anode to refine the metal at 850° and 1000° from an electrolyte of NaCl + $TiCl_3$, and the structure of the cathodic

deposit was studied [62]. With a perforated beaker of Ti as anode and a steel rod as cathode, a mixture of KCl + NaCl, to which about 5% of $TiCl_2$ + $TiCl_3$ had been added, was electrolysed at 700-800°C, at 0.5-6.2 A/cm^2. The higher the $Ti^{2+}/(Ti^{2+} + Ti^{3+})$ ratio, the better was the current efficiency -- between 63 and 98% [63]. In North America electrorefining in NaCl at ∿850°C is preferred.

In the Urals Institute, anodic dissolution of Ti was studied in fused chlorides with the addition of NaF. To an equimolal mixture of NaCl and KCl, 0.5 and 5% of $TiCl_2$ was added; in the second series of experiments, NaF was added (1-57.2% by weight). No detailed description of the results was given [64]. A series of studies has been carried out in the Al-Mg Institute as well. In principle any compound of Ti which possesses electronic or electrolytic conductance can work as a dissolving anode [65] in any electrolyte which is acidic enough in the Lewis sense to dissolve away the air-formed protective oxide. This includes, in addition to metallic Ti, its carbides, nitrides, borides and so on, and, certainly, various kinds of Ti wastes and scrap.

Several articles on producing Ti and refining it by electrolysis are published in the collection "Titan i Ego Splavy" ("Ti and Its Alloys") Vol. 6 (1961). For example, Ti produced from a molten salt mixture of chlorides of alkali or alkaline-earth metals at 700-750° is a result of a secondary process: Na or a sub-oxide of Ca reduces $TiCl_4$ to Ti chlorides of lower valency which are fairly soluble in the melt. Ti produced by this process, or out of NaCl + KCl + TiO_2 melts, needs to be refined if admixtures such as oxygen, Fe, S are to be removed [66a]. Of special interest to battery technologists may be the fact that when a Ti-Al alloy is used as an anode, pure Ti is obtained at the cathode only when the alloy contains less than 4% of Al. If the Al content is between 4 and 40%, the deposit on the cathode contains between 1% and 25% of Al. The electrolyte (chlorides) contains TiO_2 + TiO up to 3%, and the current density is up to 1 A/cm^2 [66b]. It may be possible to develop a rechargeable system based on this alloy.

Ti can be refined electrochemically from anodic material contained in a perforated basket made of non-reacting metals, or specially pressed into rods. Ti can be separated electrolytically from every metal except V and Mn; these cannot be removed during one operation [66c]. A special investigation of the electrochemical separation of Ti-Al alloys was carried out. Normally separation of those metals by conventional methods of electrolytic refining is inefficient due to the proximity of their potentials in NaCl melts. However, when $CaCl_2$ is used, in which $AlCl_3$ is sparingly soluble, then this separation becomes possible [67]. By contrast, codeposition has been widely practiced [30].

The melt used for refining Ti can be a pure alkali chloride or a mixture of alkali-and alkaline-earth chlorides. Therefore, it is necessary to control the composition of the Ti and of the steel which are used to prepare the cathode and the basket (which is filled with pieces of the refined metal or alloy) respectively, in melts which contain the lower chlorides of Ti. For example the following reaction: $Ti + 2TiCl_3 \rightleftarrows 3TiCl_2$ was reported in [68a]. The conditions of this reaction and the behaviour of a Ti-Al-Mn alloy were studied by the same author [68b]. A eutectic: $MgCl_2$ 51%, NaCl 41%, and LiCl 8% with the m.p. of 430° was found to be manageable.

The work on electrolytic winning and refining and alloy formation which started in the middle of the 1950's has been going on intensively since. Although more patents have been published on this topic in the Western World than in the U.S.S.R., the number of published papers on the electrochemistry of Ti in Russian is quite substantial. This high level of interest can be interpreted as indicating the persuasion of the Russian technologists that the electrochemical methods of producing Ti (including refining) offer the best way to decrease the price and to control the composition. Thus in Ref. [66b] it is explicitly stated, for example, that one of the basic ways to decrease the prime cost of Ti is to turn to the electrochemical method of its production. Incidently, Higbie and Wessel agree, in a recent analysis of the situation [69].

Several articles on Ti technology appear every year in the Russian J. Appl. Chem. and other periodicals. One fairly recent article on the microstructure of the electrolytes used for Ti refining discerns 3 types of such electrolytes: (a) KCl + NaCl; (b) KCl + NaCl + $MgCl_2$ (less than 10%); and (c) KCl + NaCl + $MgCl_2$ (more than 30%). All these electrolytes dissolve $TiCl_2$ and $TiCl_3$ [70]. Low melting temperatures are preferred for the reason of lower corrosive action and easier maintenance.

The difficulties of depositing a galvanic layer of Ti, due to its strong oxide film, have been overcome by the addition of fluorine-containing salts which dissolve it. In a low-melting combination of NH_4KF_2 + CH_3COONH_4, titanium is activated and acquires a negative electrochemical potential [71]. Systems of this kind, involving KHF_2, NH_4KF_2, with nitrates and salts of organic acids such as formic and acetic, might provide very useful combinations of low-melting electrolytes for batteries based on Ti. Systems of Ti salts and oxides, combined with NaCl and other chlorides of the first and second group metals (Li, K, Mg, Ca) have high melting temperatures or form two liquid layers [72a]. The ternary system $TiCl_3$-NaCl-KCl has only a small region of compositions melting below 600° [72b]. In the systems $MgCl_2$-$TiCl_2$ the liquidus curve falls smoothly from 1025° (m.p. of $TiCl_2$) to about 716°, where near the composition of pure $MgCl_2$ there is a peritectic point. In the system NaCl-$TiCl_2$ there is a eutectic at 600° [72c].

However, some low-melting systems have been found to have useful properties. Thus for the electrolytic preparation of Ti a ternary eutectic was suggested, which forms if $TiCl_3$ is added to the binary eutectic of 60 mol% of LiCl + 40 mol% of KCl (melting point of 355°). This lowers the m.p. to 343°, but above 460° two layers are formed. The electrolysis of the ternary mixture with W electrodes produced a 99% Ti deposit with 60% efficiency [73].

Several articles on electrochemical production and refining of Ti have been published during the 1950's and 1960's in the Journal of the Electrochemical Society [74] or in special editions, like those of the U.S. Bureau of Mines [75], as well as many patents. Several references are given in [2]. However, these publications do not contain new information useful in battery development, and therefore are not discussed any further in this report.

Studies connnected with electrolytic winning and refining were going on in the U.S.S.R. in the 1970's [76a,b], as well as in Japan [77].

The work seems to be continuing world-wide.

THE LITERATURE ON THE USE OF TITANIUM IN BATTERIES

In the preceding sections of this report we have considered some properties of Ti which may pre-determine the possibilities of its use as the energy source in batteries. In the present section we will summarize these properties and select some relevant literature connected with the use of Ti in batteries. In the following section we will put forward some suggestions on that topic.

PROPERTIES OF TITANIUM WHICH SUGGEST ITS USE IN BATTERIES

The energy of a battery, or of an electrochemical cell, is supplied by the reaction which takes place between its electrodes. One electrode, the anode, is usually a metal, which is oxidized by the cathode material, containing oxygen, chlorine or another oxidizing agent. The energy of this reaction, divided by the weight of the reactants, gives the theoretical energy-density (ED) of the battery. From the data of Table II it is clear that the theoretical ED of Ti cells, although lower than that of Al, Mg or Na, can be much higher than the ED of Fe, Zn, Pb and Cd cells.

Although the ED due to a given anode varies, depending on the kind of oxidizer (for example, free O_2 or Cl_2 or their compounds), the sequence or order and even the ratio of ED's of various metals remains substantially the same, as well as do their standard potentials. This can be concluded from many published sources, for example, from [78].

High potentials and ED's for Ti are deduced not only from theoretical considerations (examples in Table II) but have been found also from experiment. As it was shown earlier, potentials between 1.8 and 2.6V have been found for Ti at high temperatures in fused salts. In a mixture of chlorides of Li, K and Na at 600° the experimental data for $Ti/TiCl_2$ were found to be 2.04V, against 1.89V, the calculated value; this can be compared with 2.84V (experimental) and 2.60V (theoretical) for $Mg/MgCl_2$ and 3.22 and 3.42V for Na/NaCl [79]. So, high voltage and ED of Ti in any battery construction can be expected with some degree of certainty. The ease of formation of Ti alloys and compounds with many metals, the fact that these alloys as well as Ti carbides, hydrides, sulfides and the like can be anodically dissolved and some of them deposited at the cathode, are also strong arguments in favour of attempting to use Ti in batteries.

TABLE II

Standard Reduction Potentials at 25° (E°_{25}) of Titanium and Some Other Metals and Theoretical Energy Densities of Oxides, Fluorides and Chlorides of These Metals

Reaction	E°_{25}	TED, Wh/Kg		
		M + O	M + F	M + Cl
Na^{+1}/Na	-2.714	1873	3767	1954
Mg^{+2}/Mg	-2.37	4158	4918	1874
Al^{+3}/Al	-1.66	4609	4307	1450
Ti^{+2}/Ti	-1.63	2301	2681	1116
Zn^{+2}/Zn	-0.763	1211	2114	848
Fe^{+2}/Fe	-0.440	1057	2203	662
Cd^{+2}/Cd	-0.403	565	1246	590
Pb^{+2}/Pb	-0.126	276	752	359

It can be argued that because of passive-layer formation, which prevents the anodic dissolution of Ti, attempts to use it in batteries with aqueous electrolytes will fail, as is usually the case with Al [80]. But, as we have seen earlier, fluoride ions activate Ti in aqueous and non-aqueous solutions; and in oxide-free fused salts no passive films on Ti are formed. In short, the information on titanium electrochemistry cited in the previous sections of this report indicate the suitability of this metal for construction of batteries of high energy density. The behaviour of a Ti-Al alloy, mentioned earlier [53a] is of particular interest, as it could be dissolved on the anode and deposited at the cathode. This means that this process is indeed reversible, usable not only in a primary battery but also in a secondary one.

Preliminary experiments may prove that the most suitable electrolytes for Ti batteries can be found among molten salts. Some systems can be suggested with melting points between 100° and 300°C. A natural question arises then after such an optimistic appraisal of Ti as a source of electrochemical power: How many attempts have already been made to realize these possibilities, or at least to suggest some designs of cells based on Ti for experimental tests? A diligent search of the available literature has shown the scarcity of papers or patents dealing with the construction of Ti batteries, or with systems of cells for that purpose, although some hints on such possibilities or even appraisals of Ti as an anode for batteries can indeed be found in the literature. Sometimes only a few words are said on this topic, as, for example, in [78], where in the table "Candidates, Metal-Oxygen Systems", Ti is also inserted, accompanied by the comment: "difficult".

REFERENCES TO Ti-CONTAINING ANODES

Various "piles" or "chains" [81], or cells, which have been constructed to measure the potential of Ti cannot be taken into account, as they could hardly be looked upon as power-producing devices. These are cells which contain Ti, electrolyte and Pt or Hg. However, some of these cells, although intended for potential measurements, can serve as a model of a Ti battery such as the following: $Ti//n\text{-}H_2SO_4//Cd$ E = 0.872V or $Ti//n\text{-}H_2SO_4$ + KF//Cu E = 0.785V [81].

At greater length the use of Ti in batteries was analyzed in a Polish journal of chemical industry, under the heading "New Electrode Materials for Galvanic Cells and Batteries" [82]. In two of the three tables of the paper Ti is mentioned and its properties are compared with those of some other metals. Some excerpts from those Tables follow:

Table A

Element	Ah/kg	Ah/cm^3	E° in acid solution	E° in alkaline solution
H (liquified)	36.6	1.003	0.0	0.83
Li	3.86	2.05	3.04	3.04
Al	2.98	8.07	1.66	2.35
Ti	2.24	10.05	1.63	-
Mg	2.2	3.81	2.37	2.69
Na	1.16	1.12	2.71	2.71
Fe	0.96	7.50	0.44	0.877
Zn	0.82	5.86	0.76	1.25

Table B

Anode Material	Ah/kg	E° Acid	E° alk.	Electrolyte
Mg	2.2	2.37	2.69	$MgBr_2$ or $Mg(ClO_4)_2$
Al	2.98	1.66	1.19	$Al(ClO_4)_3 + (NH_4)_2CrO_4$
Ti	2.24	1.19	1.69	$HF + NH_4F + KCl$

Comparing Ti and Mg, the author advises attention on titanium which, with the same productivity, requires less volume and is, therefore, a more promising material.

Despite the promising title: "A Survey of the Possible Use of Ti in Batteries", a British article published in 1963 contains recommendations only for the use of Ti in the grids of storage batteries, where the mechanical properties of Ti and its resistance to corrosion can be exploited. The problem still being addressed today is to anchor a continuous deposit of Pb on Ti [83]. Again, Ti coated with Zn has been recommended for electrodes in Zn-halogen batteries in a British patent [84].

The possibility of using Ti as a battery negative is discussed by Jasinski in his book on high-energy batteries [85a]. Although the problem is complicated by protective film formation, it does not exist, it is said in some patents if alloys of Ti are used. Another approach involves the use of

aqueous fluoride media. Several patents claimed by J. McCallum and co-workers are cited [85a, p 56-57]. A U.S. patent is granted for electric current generating cells with Ti or Ti-alloy anodes and aqueous solutions of HF, NH_4F, HCl and their combinations as electrolytes. PbO_2 is recommended as a cathode in these primary cells [85b]. Another primary cell with a Ti-rich alloy as anode in a concentrated aqueous alkaline solution is claimed in three of these patents [85c].

The application of Ti for working electrode material in a battery is proposed in the paper [86] which indicates the use of titanium and zirconium only as primary-cell anodes. Both these metals have large negative electrode potentials and relatively low equivalent weights and volumes. The passivity of Ti could be eliminated by H_2SO_4 above 5%, by H_3PO_4 above 30%, by certain organic acids and by HF at all concentrations. Thus addition of NH_4F increases the dissolution rate of Ti in HCl and H_2SO_4 up to a concentration of 4N-NH_4F, above which Ti becomes passive, while NH_4F reduces the rate of dissolution in HF. Ti costs $\sim$ \$2.05/lb. The E° for $Ti/TiCl_2$ is 1.19V. Cells recommended are of Ti or Zr as anode and either $Pb-PbO_2$ or $C-MnO_2$ as cathode. The electrolytes suggested are H_3PO_4, HF, H_2SO_4, $FeCl_3$, NH_4F and combinations of these [86].

A Ti/Cl_2 primary battery incorporating a molten chloride electrolyte was proposed in a French patent in 1974 [87].

No papers or patents on Ti batteries of any kind have been published up to late 1973 in the U.S.S.R. However, the paper [88], according to its title, deals with corrosion and electrochemical behaviour of Ti in solutions of KOH, KOH + LiOH and H_2SO_4, but it starts with the following sentence: "The possibility of using Ti in chemical sources of power has been considered by several researchers". Among these, reference [86] is cited, along with a book of N. Tomashov on corrosion and protection of Ti (1963), and a collection of articles: "Advances in Chemical Sources of Power", which is issued by the Soviet Battery Institute, and, evidently, not available outside Russia. One of the leading personalties of this institute is M.A. Dasoyan, who is also a co-author of [88], which is related to the work carried out, in this Institute, on Ti batteries. It can be regarded, together with some other papers published in Russian journals during the last years, especially in the "Zhurnal Prikladnoi Khimii" on the electrochemistry of Ti, as a welcome sign of Soviet work on Ti batteries. A few further notes from the paper [88] follow: Ti of 99% purity shows in 10N-KOH, E = -1.15V at 20° and does not become passive. In KOH + LiOH strong passivation occurs, as a film of LiOH is formed. In 8N-H_2SO_4, the potential of Ti is -0.301V and it becomes more positive with rising temperature [88].

Titanium hydride, the composition of which is close to the formula TiH_2, contains about 4% of hydrogen. It is inert to air, water and most acids and decomposes slowly at 400°C. As its heat of formation is only -34.5 Kcal/mole (-29.5 Kcal/mole according to [89a]), both its components may serve as anode materials. It had found several applications and is available as a commercial product [89]. Articles and patents on the use of Ti hydride as anodes have recently been published.

The anodic dissolution of Ti hydride and alloys in non-aqueous media was studied as a means to separate the hydride from other metallic phases [35]. In the Moscow Research Institute of Power Sources intensive work on batteries with anodes of Ti and Ti-Ni hydrides is carried out under the guidance of the director of the Institute, Associate Member of the U.S.S.R. Academy of Sciences, N.S. Lidorenko. The hydrogen-absorbing capacity of some Ti alloys and of the intermetallic compounds in the system Ti-Ni has been studied, as well as the electrochemical properties. Storage batteries with the Ni-Ti anodes have been prepared, and their cycle life studied, and the results compared with the relevant data of the Ni-Cd, H_2-O_2, and Ni-H_2 systems [90]. In the charging cycle the Ni-Ti alloy absorbs hydrogen, which works in the anode during discharge. In parallel with that work, many studies of electrodeposition of Ti alloys on the cathode from various electrolytes should be taken into account. Several such works were published in the U.S.S.R., as, for example, a patent on an alkaline bath for Ti alloys deposition [91], and a report on the Ti-Ni alloy electrodeposition from an aqueous H_2SO_4 solution [92]. Among the Ti-Ni alloys, the anodic behaviour of which in KOH and H_2SO_4 solutions has been studied, were also those with 33 atom % of Ni, the compositions of which are close to that of the intermetallic compound, Ti Ni known for its high absorption of H_2 [93].

Several publications on Ti-hydride anodes have appeared recently in the Western countries. The alloy-hydrogen reactions are being applied to hydrogen storage. Examples include: ternary Ti hydrides ($ZnTiH_2$, $FeTiH_2$) [94], and $FeTiH_2$ in [95]. Although these hydrides are considered as candidates for hydrogen storage, they may also find applications for anodes in storage batteries.

The idea of developing secondary cells based on reversible hydrogen transfer between electrodes capable of absorbing large volumes of H_2 in interstitial solid solutions is discussed in [96].

In a British patent a battery with an anode of TiH_2 is described, and a fuel cell attached to the battery has the same anode. The ED of the battery is higher than 140 Wh/kg and it could be considered for electric vehicles [97].

The preparation of storage-battery electrodes with the ability to accumulate hydrogen is described in a French patent. A Ti-Ni hydride is given as an example [98]. The importance of the Ti hydrides as anodes for batteries can be inferred from the fact that according to [95a] the ED of $FeTiH_{1.95}$, only on the basis of the available hydrogen, is 268 Wh/lb (590 Wh/kg). This value will increase, if the participation of Ti in the redox reaction is taken into account.

Other Ti alloys may also be suitable. The alloying metal can be chosen whether to eliminate the passivity of Ti or to moderate (and sometimes to enhance) its anodic dissolution. The chances of reversibility could also be increased by alloying. Aluminium is one such useful metal, and it is mentioned, together with Mo, Nb, and Zr in [85a].

TITANIUM COMPOUNDS AS CATHODES

Titanium sulfides, along with sulfides of other transition metals, have been proposed recently as cathodic materials for batteries with light metal anodes.

Cells of the type: Na/propylene carbonate NaI/TiS_x were studied. to obtain thermodynamic data. In other cells Li and K were used [99].

The charge-discharge process in a cell: Li/Li salt in propylene carbonate/TiS_x with TiS_2 and TiS_3 were discussed in [100]. Trumbore, Broadhead and co-workers have issued several publications on transition metal chalcogenides used as cathode materials for lithium-non-aqueous batteries. Preparation of fibrous films of these chalcogenides is described and the capacities of Li non-aqueous cells with cathodes of films of Nb, Ta and Ti sulfides and selenides were studied [101]. The cyclic behaviour of these cells with NbS_3, $NbSe_3$, $TaSe_3$ and TiS_3 was reported [102a], and the prospects of such batteries were discussed at length [102b,c]. During the studies of Li-non-aqueous cells with TiS_3 and $NbSe_3$ cathodes, it was found that whereas the cell reaction is reversible for $NbSe_3$, it is only partially reversible for TiS_3. However, despite the alleged partial reversibility of the TiS_3 cathode, it is recommended, along with Nb and Ta chalconides, for Li-non-aqueous batteries in a patent [103] claimed by the authors of [101].

Stressing the role of ternary phases in cathode behaviour, Whittingham has considered five possible reactions between a Li anode and a TiS_2 cathode. The reaction leading to the formation of Li_xTiS_2, where $0< x <1$ seems the most probable, with better chance of reversibility [104a]. A new battery system is based on this reversible reaction. The relationship between intercalation chemistry and electrical energy storage is discussed in [104b].

SOME SUGGESTED TITANIUM BATTERIES

In the previous sections of this report we have examined the potential of titanium in batteries by its abundance, availability, and by the

comparison of its EMF and TED with the values of these properties of metals used in conventional and promising storage batteries. The studies of the electrochemical properties of titanium, which have been carried out during the work on its winning, refining, corrosion and electroplating, have provided ample starting material for the research on titanium batteries, which has started recently. We now summarize the previous sections with an appreciation of the use of Ti for anodes and cathodes in storage batteries, adding a few remarks on appropriate electrolytes.

Ti AND Ti-ALLOYS AS ANODES

Whether we will use anodes of pure titanium or of its alloys and hydrides, the proper choice of cathodes is important.

The function of the cathode is to deliver the oxidizing material, which can be either in the elemental state, as Cl_2, O_2, Br_2 and S, or as a compound with a metal. The disadvantages of the compound cathodes are: (a) the increase of the cell's weight by the metal part, and (b) the decrease of the cell's energy by an amount equal to the energy of reaction of the cathodic metal with the oxidizer. Both these factors decrease the ED of the cell. Although an elemental oxidizer does not possess these disadvantages, it presents another, formidable, problem, viz. the retention at the cathode of oxidizers like O_2 or Cl_2, which are in the gaseous state at ambient temperatures. See Reference [87].

From the comparison of the TED of couples formed by Ti with elemental oxidizers, we can clearly see the advantage of a Ti anode over the heavy metal anodes. The TED and the $E°_{25}$ of cells formed by Ti with O_2, F_2 and Cl_2, being lower than those for Al and Mg, are much higher than the TED not only of Fe, Cd and Pb -- the anodes of conventional storage batteries -- but even of Zn -- the most active heavy metal. For the reaction M + O, the TED of Ti is even higher than that for Na. As the use of the elemental oxidants, due to their gaseous state, poses difficulties for recharging, they are usually replaced by their compounds -- oxides, chlorides and so on. However, in this case too Ti preserves its intermediate position between the light and the heavy metals. This can be seen, for example, from Table III, where the TED for cells with the chlorides of Cu, Ni and Fe as cathodes are presented. The TED's for Ti cells are between 1.5 and 2 times the corresponding values for Zn cells, and are at least as high as the respective values for Al cells. Thus, Ti has a good a chance to be accepted for use in primary and secondary batteries as does Zn.

Some metal halides or oxides which are formed with a small energy of formation might best be used for a secondary Ti battery. Thus for a hypothetical Ti-$CuCl_2$ cell:

TABLE III

Theoretical Energy Density of Displacement Reactions:

$$M_I + M_{II}Cl_x \rightarrow M_ICl_x + M_{II}$$

where M_I = light metal, Ti, Zn

and M_{II} = Cu, Ni, Fe

M_I	Valency	TED, Wh/kg		
		$CuCl_2$	$NiCl_2$	$FeCl_2$
Li	1	1198	1050	972
Na	1	957	804	780
Mg	2	761	601	534
Ca	2	921	801	773
Al	3	478	296	232
Ti	2	469	308	277
Zn	2	292	151	116

$$CuCl_2 \rightarrow Cu + Cl_2 - 49.2 \quad Kcal \qquad (1)$$

$$Ti + Cl_2 \rightarrow TiCl_2 + 122.8 \quad Kcal \qquad (2)$$

$$Ti + CuCl_2 \rightarrow TiCl_2 + Cu + 73.6 \quad Kcal \qquad (3)$$

73.6 Kcal = 85.6 wh, which being divided by 47.90 + 134.45 = 182.35g or 0.182 kg (the mol. weights of Ti + $CuCl_2$) will result in 469 wh/kg. This theoretical energy density (TED) will be reduced 10-20% by the weight of the electrolyte.

Other cells could also be proposed using Cu compounds, for example with CuF which offers a TED of 553 wh/kg, close to that of a Ag-Zn battery; or with CuO, which offers a TED of 797 wh/kg. The chloride or oxides of Fe, Ni, Co and Mn could be considered as well (Table III).

When free chlorine is delivered (eq. (2) above) the TED of the battery will be 1203 wh/kg, i.e. about five times that of the Pb-acid or the Ni-Cd, or >2 times that of the Ag-Zn battery. Absorbents for Cl_2 can be introduced, or Br_2 or S could be used as cathode materials, but the energy density must be lower as a result.

These energy-densities are quite significant. Moreover, even higher values, based on the formation and stabilization of positive plate material composed of Cu^{+3} or Ti^{+6} compounds in molten salt electrolytes are not impossible. Root et al. have stabilized $[CuF_6]^{-3}$ in flinak [105] (the eutectic mixture of the chlorides of lithium, sodium and potassium), and the Pourbaix diagram predicts stability of TiO_3 above 3 volts. TiS_3 is known; it might be stable and electrochemically active under some conditions.

Perhaps something could be done with the Ti nitride, the electrochemical behaviour of which in chloride melts was reported in [56]. Like the Zn-air battery which utilizes oxygen from the air [106], perhaps it would be possible to utilize the nitrogen to form the nitride in some electrolyte. Similarly, the phosphide has already been shown [107] to be formed and to be remarkably electrochemically reversible in molten metaphosphate; it may have the desirable properties in more highly conductive melts.

Titanium hydrides can be used as anode in a reversible cell. Thus during electrolysis of aqueous solutions with Ti and Ti-alloy cathodes the cathode absorbs substantial amounts of hydrogen [108]; this fact offers the promise of its operation as an anode during the subsequent discharge of the cell.

Ti COMPOUNDS AS CATHODE MATERIALS

Experimental work on batteries with Ti compounds as cathodes [101-104] have been discussed earlier in this report. As there are several possibilities of reductions of titanium from a higher valency to a lower one, various EDs can be obtained for the same anode, depending on the valency changes in the cathode material. In Table IV the theoretical ED's of cells with light metals (and Zn) anodes and with the TiS_x cathodes are presented. Higher ED's can be obtained with TiS_2 than with TiS, because the bond-strength in the latter compound is the higher. The ED values for Li, Na, Mg and Ca are sufficiently high (but not for Na and Mg with TiS) to warrant experimental study of these couples, whereas for the Al and Zn couples these values are too low. The negative signs for Al and Zn show that in such couples these metals would play the role of the positive plate, during discharge, and the TiS_2 would be the negative.

The value 348 Wh/kg for $TiS_2 \rightarrow TiS$ and Ti shows that, in the cell Ti/TiS , titanium will be negative if the cathodic reaction is $TiS_2 \rightarrow TiS$. This fact opens the vistas for several combinations of the reactants in cells in which other compounds of Ti_{IV} as cathodic materials react with an anode of metallic Ti (Table V). Apart from the Ti/TiS_2 couple, other cells based on the reaction:

$$Ti + TiX_n \rightarrow 2TiX_{\frac{n}{2}}$$

can be realized, where X = O,Cl, Br, Se and so on. In the case of oxygen the reaction is analogous to that of the conventional lead-acid battery. Although the ED of the reaction $Ti + TiO_2 \rightarrow 2TiO$ is low (208 wh/kg) it is still higher than the respective reaction for $Pb + PbO_2$. If the energy of the reaction $2TiO + 2H_2SO_4 \rightarrow 2TiSO_4 + 2H_2O$ is added (the value is certainly higher than for the respective Pb reaction), the ED for the "titanium-acid" storage battery will be greater than 352 Wh/kg (Table V).

The compound TiS_3 is also mentioned in the literature as a cathodic material [101] but reliable data on the energy of its formation and decomposition are not available. FeS_2 is similarly undefined. However both these compounds are of interest as cathodic materials, not only coupled with Li or Na, but also with Ti.

TABLE IV

Theoretical Energy Density of Cells with Titanium Sulfide Cathodes

Anode	Valency	TED, Wh/kg		
		$TiS_2 \rightarrow TiS$	$TiS_2 \rightarrow Ti$	$TiS \rightarrow Ti$
Li	1	848	1165	545
Na	1	399	446	140
Mg	2	485	476	104
Ca	2	681	787	400
Al	3	273	104	-153
Ti	2	348	-	-
Zn	2	145	-33	-212

TABLE V

Theoretical Energy Density of Cells: $Ti + TX_n = 2TiX_{\frac{n}{2}}$

(as compared to the Pb-acid cell)

	Cell	TED, Wh/kg
	$Ti + TiCl_4 = 2TiCl_2$	275
	$Ti + TiS_2 = 2TiS$	348
	$Ti + TiO_2 = 2TiO$	208
+	$Pb + PbO = 2PbO$	103
	$2PbO + 2H_2SO_4 = 2PbSO_4 + 2H_2O$	144
	$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$	247
	$Ti + TiO_2 = 2TiO$	208
+	$2TiO + 2H_2SO_4 = 2TiSO_4 + 2H_2O$	> 144
	$Ti + TiO_2 + 2H_2SO_4 = 2TiSO_4 + 2H_2O$	> 352

ELECTROLYTES

In most commercially available batteries, primary and secondary, now in use, aqueous solutions serve as electrolytes. Non-aqueous and fused salt electrolytes are exceptional in practice. The disadvantage of non-aqueous solutions is their low conductance, and the fused salt electrolyte cells work only at elevated temperatures. However, there are several conditions where non-aqueous and fused salt media are used, and the new battery candidates using Na and Li in these electrolytes are becoming available.

In aqueous solutions the attempts to use Ti will undoubtedly encounter the same difficulties as are encountered with Al or Mg, either passivity or rapid dissolution. Non-aqueous solutions may be more advantageous, or an organic electrolyte to which some small percentage of water is added. Such an electrolyte might be appropriate for TiH_2, which gives, with a NiO cathode, a TED of 140 wh/kg, according to [97].

There is a group of solutions that can be considered as intermediate or transitional between non-aqueous media and fused salts. They are better conductors than the former and have lower melting temperatures than the latter. These are systems composed of nitrates, acetates and formates of the alkali and alkaline-earth metals [109]. Further electrolytes containing $TiCl_4$, $NbCl_5$ and $POCl_3$, which are liquid even at ambient temperatures could be considered [110]. However, the stability of these materials in the presence of anode and cathode might be inadequate.

Other low-melting systems are formed by mixing Fe-or Al-halogenides with halogenides of Groups I and II. Thus a mixture of 20-30% of NaCl + 80-70% of $FeCl_3$ melts at 160°C. The anodic reaction product of Ti is not likely to cause passivation. The reaction of Ti with $FeCl_2$ has already been studied as a refining process; metallic Fe is displaced by metallic Ti:

$$Ti + FeCl_2 \rightarrow TiCl_2 + Fe \quad [111].$$

If used as an electrochemical cell, it will have a ED of about 278 wh/kg. The analogous system with $FeCl_3$ would give an TED of 386 wh/kg, much higher than that of conventional Ni and Pb batteries.

Amongst the low-temperature melts (300-500°C), the ternary chlorides with or without the addition of fluorides stand out as candidate electrolytes for rechargeable battery systems. Stabilization of a reversible HED cathode material will be the critical problem.

Cryolite-like baths for reversible operation of the Ti/Ti^{2+} couple must be hot. Thus Ti has been deposited from a mixture of alkali chlorides at 600°C [79]. Ti coatings can be deposited on steel cathodes in fused salts while Ti is being dissolved at the anode at 750-850°C, the best results to

date having been obtained from a bath containing KI, KF and TiI_4 [112]. Reference has been made to the alkali chloride electrolytes used in refining, and to the alkali fluorides used in electroplating. The processes run hot, 650-900°C.

The review of Strivastava and Muckerjee [30] suggests some other electrolytes needing study from the point of view of co-deposition of the Ti with other metals from mixed molten-salt electrolytes at lower temperatures.

Whatever the electrolyte, it seems axiomatic that the storage of charge at the cathode will be more difficult, the higher the temperature. Electrolytes chosen to facilitate reversibility at the negative often are unsuitable for the positive -- and vice versa.

It is curious that the possibilities offered by anhydrous sulfuric acid as electrolyte in practical rechargeable systems have not been addressed in the literature. Is this simply an oversight?

Table VI gives some cells which warrant experimental investigation.

GENERAL CONCLUSION

The fact that only a few publications can be found on the use of Ti in electrochemical power cells is related to the peculiar history of the availability of Ti. It was relatively recently that Ti metal became available for technical use, attention having been diverted toward methods of production and refining. Today Ti has become a commercial metal. A substantial amount of information on the electrochemical properties of the metal and its salts and oxides in various media has been accumulated. Hence, it is very timely to initiate intensive studies on the use of the metal and its compounds in batteries. From the available literature one can readily infer that such studies are already being carried out in several countries and one can predict that a rash of publications and patents on work directed towards this end will appear during the next ten years.

Titanium possesses properties which could provide a basis for high energy density primary and secondary batteries, as well as for electrochemical cells for special kinds of services. However, a substantial amount of research and development must be performed to achieve the realization of this goal.

TABLE VI

Several Titanium Battery Concepts

					T(°C)	Type*
Aqueous Cells						
Ti	//	Strong H_2SO_4	//	PbO_2,Ti	-40 to RT	P
Non-Aqueous Cells						
Ti	//	Anhydrous H_2SO_4	//	TiO_2,Ti	10-100	U
Li	//	$LiPF_6$ in PC	//	TiS_2	20-60	S
Melted Salt Cells						
Ti	//	$NaTiAlCl_6$	//	MoS_2	100-200	S
Ti	//	$Na_2TiNiCl_6$	//	Ni_xP	300-400	U
Ti	//	alkali halide eutectic Cl^- F^-	//	X or $[TiX_n]^{-m}$	350	P
					550	S
Ti	//	NaCl	//	Cl_2	850	P

* P - primary
S - secondary
U - unknown

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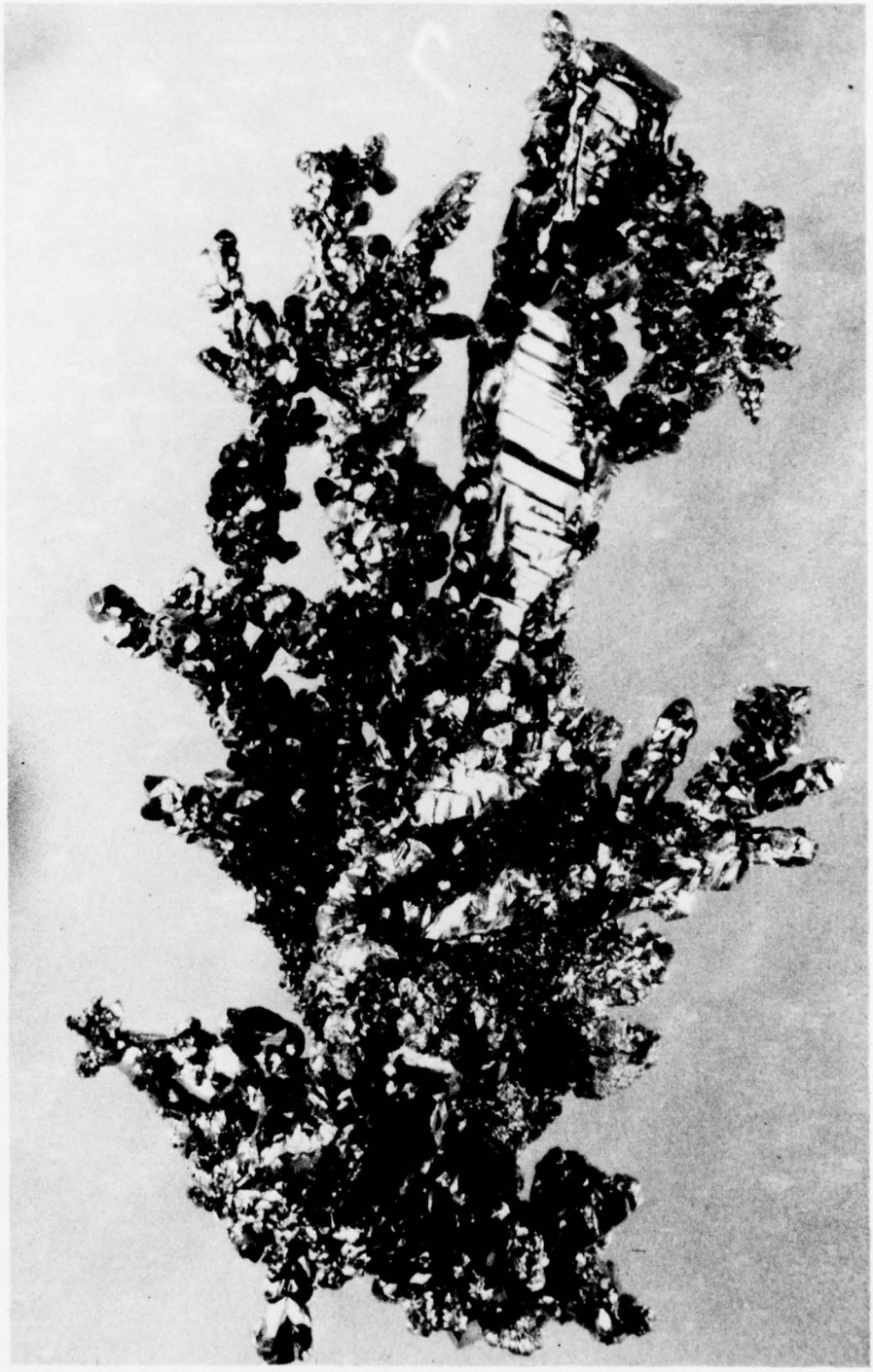

Fig. 1: Refined Titanium Dendrite (2x). Courtesy of J.C. Priscu, Titanium Metal Corporation of America, Henderson, Nevada.

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Titanium has become available as a commercial metal only since World War II, and, at low price, a decade later. This explains the fact that Ti has not been utilized as a reactant or energy-supplying material in batteries, despite its advantageous properties -- its low weight-density and the high energy-density of its reaction with oxygen and halogens.

After a review of the occurrence and technology of titanium, the history of its studies in the USA and in the U.S.S.R., its electrochemical behaviour in aqueous and non-aqueous and molten salt media is discussed. Suggestions on the choice of materials for anodes, cathodes and electrolytes for Ti batteries are presented and several electrochemical reactions on which these batteries are based are offered.

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