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REFLECTIONS ON SOME RECENT STUDIES OF MATERIALS OF IMPORTANCE
 IN AQUEOUS ELECTROCHEMICAL ENERGY-STORAGE SYSTEMS

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1. INTRODUCTION

Delineation

In this paper an attempt is made to provoke thought on materials which are used or are formed in rechargeable batteries based on watery electrolytes. It was decided not to attempt a compendium, but rather to focus in on selected topics which in our judgment seem important and on which new information has a good probability of practical payoff in improved performance.

By performance here are meant the usual measurables:- For rechargeable cells: nominal energy-density by some selected criteria; turn-around efficiency and realizable energy-density as measured under a selected cycling regime; energy-retention during a cycling regime chosen to simulate some operational mode; incidence and types of failure; reconditioning-ability and repairability. For fuel cells: efficiency of conversion at a power density acceptable for the application; mean-time between failures; reconditioning ability and repairability.

To the user, especially the user who has an important tactical mission to achieve, the ability to recondition or repair --

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ideally of course the elimination of the necessity to do so -- is often more important than other considerations. Reliability and longevity are assigned high places amongst performance criteria. Reliability and longevity should not be confused, although they are often interrelated manifestations of performance, equally dependent upon materials-selection and upon quality-control during manufacture.

Philosophical Focus

Three major questions are considered:

1. What use are we really making of the information resulting from techniques which have become so popular in recent years?
2. What information are we lacking which would enable us to make major improvements in performance?
3. What basic assumptions about systems are we making which should be challenged?

In this paper these questions are not treated systematically, or separately, one from the other, but they underlie all of the discussion to follow. "What problems demand our attention?" "If we worked on a particular problem, using certain tools, are we likely to be able to use the results in some practical way?"

This paper contains no discussion on many practical problems having fundamental overtones and concerning the systems now in use or being readied for introduction into the marketplace. We make little comment on topics such as: (a) Lighter supporting structures for the active masses in lead-acid battery plates, or the selection and characterization of suitable oxides; (b) Separator materials which will be chemically stable and will defeat the run-away (burnout) problem in the nickel-cadmium and silver-zinc systems during overcharge; (c) Long-lived and efficient air electrodes for air batteries and fuel cells; (d) Shape changes at the non-oscillating zinc plate in nickel-zinc batteries; (e) Adaptation of lead chloride for more extensive use in a variety of sea-water batteries. These topics are indeed of great practical importance even to the non-military user; and although our Laboratory has been working in most of these areas, it is not our intention here to focus on them. Let our only example be to mention the replacement of the scarce silver salt by cheap lead chloride in the seawater batteries which are now used by the thousands in most passive sonobuoys. Coleman and King did the pioneering work (1a), and others have followed it up (1b).

Further, the organizers of this Institute have invited us, indeed challenged us to stick with aqueous systems, and to try to say interesting and useful information about them. This proscription should not be interpreted as indicating that our Laboratory does not have interest in non-aqueous, molten salt and solid-polymer electrolyte systems. Indeed there is strong interest, because many new applications of the new systems can be envisaged. Much of our research effort currently is directed to these other battery systems.

Neither do we include a comparison of the state of the development of the fifty or so electrochemical couples which are receiving attention in the many laboratories engaged in research and development, world-wide. Each credible consultant or specialist in this field has his own good sources and resources, and no attempt is made here to produce yet another primer for the battery engineer. Many comparative reviews exist, but computerized expression of what system might be best for any given application is not highly developed yet.

We decided to offer information from our own research directed towards real problems facing our customers in the Canadian military community. Our collective goal surely, with rising costs of research, must be to improve our chances of coming up with practical information which will enable ourselves and our colleagues in industry to bring new and improved systems more rapidly to the marketplace for application.

Inclusions

Following this Introduction, five general topics selected for discussion in this paper are treated in the following order:

Deteriorating Water Quality -- (A Cause that Defreshes)
Photoactivity -- (New Light on Surface Phenomena)
Transition Region Electrolytes -- (Almost Out of Bounds)
Electrochemical Spectroscopy -- (The New Optic)
Techniques and Materials -- (The Chronic Problems)

These topics reflect some of the current interests of colleagues at DREO. The references to their work and to that of the author are intended to promote contacts with others who are interested in these same subjects.

11. DETERIORATING WATER QUALITY

New materials are entering the surface water world-wide, some

carried by rainfall, some as waste-water from domestic or industrial use and some from modern plumbing materials. Salts, organic materials and unnatural (perhaps redundant) synthetics are decreasing the purity of the water which is used as the source of electrolytes for all aqueous electrolytic cells. Some of these additions are hard to detect, let alone identify, and may persist through the various purification processes which the water undergoes before it finally enters the electrochemical cell. In Canada, polychlorinated biphenyls are found in the rain and rivers which feed the Great Lakes. Polyethylene has been found in the mid-Atlantic and in lab plumbing. Traces of chloroform have been reported in the water supplies of many Canadian and other cities. These products and motes of all sorts (finely dispersed inorganics, spores, etc.) can persist through most of the purification processes which the water undergoes before it finally enters the electrochemical cell.

Years went by before the purity of the water which is used as the source of electrolytes for all aqueous electrolytic cells, batteries and fuel cells was suspected. Many of the organic compounds as added or as altered pass through ordinary distillation and even from alkaline permanganate. Criddle (2) early recognized this problem and devised a preparative procedure for "pure water" which is low in surface-active organics, products of biodegradation and stray inorganics and motes unwittingly introduced by the removal procedures and equipment themselves.

Pyrodistillation is the key new process: it includes oxidative pyrolysis of water vapour, to destroy the organic impurities of water vapour, and careful redistillation. With pyrodistilled water researchers (2) have been able to make up experimental cells which show much less evidence of poisons adsorbing gradually on the surfaces under examination. The process of Reverse Osmosis, using membranes of carefully selected and controlled chemical composition and physical properties, can produce purified water of outstanding quality. Deionizers help--or do they? How many of us really do know the quality of the water used in preparative procedures in our own laboratories? Just imagine how important the procedures quality-control should be in processing industries in which battery materials are fabricated and assembled. Without pure water, even researchers are still plagued with irreproducibility....With such variability in the surface waters of the earth, no wonder battery cells from different countries can show such variation.

Sometimes the persistence of poisons can be correlated with the infrared spectra of the evaporated residue -- there should be

no residue and no spectrum, of course, but preparative procedures very often fail. One asks: Is it the care by the researcher, or is it the difficulty of getting the water to separate from the impurity, which is failing? In our experience, it is both. In our Laboratory we have found it extremely difficult to remove impurities and to keep them out. In crude experiments with complete alkali batteries the purity does not seem to be crucial. However, when exhaustive performance is intended -- at low temperatures and high power levels for example -- water quality must be assured, otherwise "oils" which have inadvertently been allowed to enter into the cells, may even cause stable foams which can eject electrolyte from gassing cells.

The effects of insufficient attention to air-quality can often be overcome by sufficient flushing, or electrochemical working, of the cell after closure, but such procedures are none too sure either. Microporous filters remove some particulates but not all. Pyrolysis can remove the organic-spore type, but other solids get through and eventually can show up on the electrode in the double layer and participate in the process under observation, usually to degrade the performance.

This problem of purity of watery solutions should not offer the non-aqueous researcher any consolation, for "oils" can be introduced into non-aqueous cells during the preparative techniques used for electrodes, chemicals, separators and seals, and the assembly of non-aqueous cells, just as easily, perhaps even more easily, than in the aqueous electrolytes under discussion here.

One can surmise that the careful researcher will be rewarded with new observations on the behaviour of the tried-but-true conventional systems when he realizes that the quality of his own water is deteriorating as a starting material, as well as that of others who process his components. More painstaking care than ever is now necessary. One must remember that Criddle did make a series of 1.6-volt oxygen-platinum electrodes fifteen years ago (Electrochim. Acta, 9, 853 (1964)), by working in wintry air that was free of enzyme producing plants and by classic distillation of deep well water from which surface waters had been excluded by ground frost.

Since DREO introduced plastic plumbing materials, the really careful researchers have had to cope with new impurities. Let us now all be more aware of "oils" in the distilled water. In our view carefully pyrolyzed water should be used for every critical and baseline experiment.

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III. PHOTOELECTROCHEMICAL PROCESSES ON BATTERY MATERIALS?

Photoassisted electrolysis of water was first reported in 1974. The prospect of practical photoassisted electrolysis has excited researchers world-wide. Even in Canada no fewer than nine research teams are active on some aspect of the phenomenon this year.

Photo-effects on electrode reactions had been observed a good many times before and, of course, up-to-date books are available (Eg. Gurevich et al., Photoelectrochemistry, Plenum Publ. Corp., NY, 1979). Some effects have practical interest. Thus color changes accompanying charge acceptance by vanadates and tungstate bronzes have elicited some interest for possible display devices. Electrolytic generation of beautifully colored polymeric intermediates, and electrochemiluminescent phenomena both caused a stir for awhile and some practical devices have resulted. The photoactivation of organic molecules absorbed on electrodes and undergoing electrooxidation or reduction receives continuing attention, as new and useful synthetic routes are sought. Photostimulated electron-ejection into electrolytes has been avidly studied by some researchers, who have been concurrently examining the surface composition by ellipsometry.

On certain surface sites of semiconductors with the right band-gap, photons can generate electrons and positive holes and separate them so that they can take different reaction paths, the electrons to reduce protons, or the holes to oxidize hydroxyl-ions in the electrolyte. The first observations of photoassisted electrolysis were made on TiO_2 electrodes.

For some years corrosion and erosion of the surface of the TiO_2 semi-conductor, under conditions of photoactivation of either the oxidation process (to O_2) or reduction (to H_2) process of water, seemed inevitable. Instability and degradation of performance resulted from continuous operation. However, it has been found that additions, particularly of soluble sulfides, to the electrolyte offer an alternative to the corrosion process. Secondly, dopants to the semiconductor have been found which move the wavelength of maximum absorption into the visible, and nearer to the solar maximum wavelength. Thirdly, in at least one case, GaAs, it has been found that the rapid surface-recombination of photogenerated electrons and holes can be inhibited by the addition of ruthenium sulfate to the electrolyte -- and the conversion efficiency greatly improved. Along with colleagues (3a), Snelling et al. (3b) at DREO have attempted to apply some of these findings to the CdSe and to CdS systems, for someone has to learn how to solve these problems and others without using the scarce gallium or the poisonous arsenic or the scarce ruthenium, if practical hydrogen production or photoelectrochemical

conversion and storage of solar energy at the practical level is to be achieved. Although other problems must be overcome before photoelectrochemical conversion can be realized -- such as: (1) identification of a cheap and reliable photoelectrode production technique, (2) long-term stability (or simple regeneration) of the photoelectrodes, and (3) identification of more suitable stabilizing electrolytes than polysulfides (See Heller, *Electrochim. Acta*, in press) -- an excellent foundation now exists for the application of these principles in other areas.

Application of these techniques and ideas to electrocatalysts and to the study of aqueous battery electrode materials has scarcely been started. Our own interest quickened when Brossard et al. (4) confirmed Pavlov's observation that the rate (current) of anodic formation of, and cathodic reduction of, thin films of PbO_2 on Pb in aqueous H_2SO_4 is markedly photosensitive under some conditions.

It is not the photosensitivity itself which is important in this case. Rather the photosensitivity, if it is not due to thermal effects, can be diagnostic. It could be telling us that we have been searching in the wrong direction in our attempts to modify the positive plate structure and composition so as to improve the charge acceptance -- rate as well as quantity accepted -- at low temperatures. Battery plates themselves, of course, cannot be photosensitive at all, unless mass-transfer along the tortuous porous structure is not rate-determining, or unless the pores and the lead-sulfate crystals are translucent.

At this stage one can only imagine what new information might be obtained if we began to use pulse-electrochemical AND pulse-photo techniques, simultaneously, on working electrodes. From the work of Langhus and Wilson (*Anal. Chem.* 51, 1134 (1979)) one can see that it should be possible to sort out the change in number and kind of charge carriers induced in the M/MO_x electrode during oxidation or reduction, when monochromatic coherent light, which has the same wavelength as the band-gap, is pulsed on and off. The most interesting results would be those which indicate whether and/or to what extent the MO_x is changing in this respect during charging/discharging. Given some ideas about what charge carriers are important, it might be possible to inject dopants which could promote more complete oxidation/reduction of the active material, and thereby improve the charge storage per gram, as well as the turn-around efficiency at higher cycling rates.

One concludes that it is not altogether trite to view photoelectrochemical techniques as "the new light" on electrochemical interface phenomena.

IV. TRANSITION REGION ELECTROLYTES

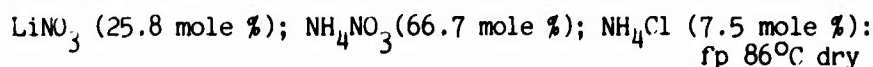
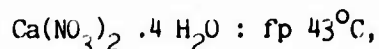
This is the most speculative part of this paper, in that, although the indirect evidence that this might be the way to go if new secondary battery systems of high energy density are to be developed, there is no experimental evidence on even one total battery system that could be considered the breakthrough which convinces.

The Transition Region has been defined and described by Klovko et al. (7) as the region of composition in which the solvent is small (present generally to less than 5 mole percent) and the molecular structure and properties are principally those of the solute. Limited, in this paper, to aqueous systems, transition-region electrolytes are simply moist salts, acids or bases which are in the liquid state, or perhaps as glassy solids.

The liquid state may begin at a surprisingly low temperature. The conductivity of the liquid generally is high. The chemical activity of the solvent -- in this case water -- is quite low. Chemical affinity of the light alkali and alkaline earth metals for the electrolyte is relatively low, and as a result these active metals can be "domesticated". Uncommon metals or plastics should not be required for the container or metallic contacts.

Light alkali metals are tame in aqueous solutions in which the concentration ratio of ions to water molecules approaches or exceeds unity. Both Li and Na have been shown to be workable as tame anodes in such very highly concentrated aqueous electrolytes. However, the electrodeposition of Li^+ or Na^+ from moist salts, acids and bases has not been investigated to any useful extent; few researchers have thought it likely enough to be rewarding even to try.

Conductivities, viscosities and densities are known for many low-melting hydrates, binaries, ternaries and other combinations of complex ions. Two examples will suffice:



In the first, there is some evidence that calcium electro-deposition is possible, and the nitrate should be reducible. In the second, reduction of the nitrate is possible, as is reformation by reoxidation, and reduction of the lithium ion may be possible without destruction of the ammonium ion. The oxidation

of lithium probably would proceed without incident. These systems need to be investigated.

The moist-electrolyte system based on equimolar KOH-NaOH gives transition-region electrolytes which are liquids from 25 to 200° depending upon the amount of water added. The interesting ones are the low-moisture electrolytes, from which Na⁺ might be electrodeposited and in which an oxide clathrate like MoO₃ might be able to be cycled.

Anhydrous sulfuric acid also has phenomenally high electrolytic conductivity due to self-ionization and hydrogen-bridge formation. Moisture affects the conductivity but very little.

Klochko (5) has pointed out other possibilities based on moist bases or on moist acids, in which the chemical activities of the water are low enough that the essential processes of charge and discharge should be able to proceed without interference from side reactions. M. Abraham and his students at U. de Montréal are actively engaged in measurements of conductivity, density and viscosity of electrolytes in the transition region, and A.N. Campbell, U of Manitoba, retains his interest and productivity in logging baseline data in this area.

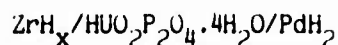
The impossibility of the applicability of dilute-electrolyte theories to the transition-region electrolytes and the lack of a good theory based on molten-salt complex theory, has probably discouraged many teachers from directing students into investigations of the transition-region. Because suitably trained investigators have been lacking, the battery community as a whole has not searched amongst transition-region electrolytes for interesting rechargeable systems. Excellent wide-open opportunities probably exist.

Some slight evidence is accumulating that some moisture is actually essential for the electrodeposition of lithium in non-aqueous systems. If this finding is confirmed, the search of the transition region becomes more cogent.

Further, the rechargeability of sodium and lithium in certain solid-polymer-electrolyte cells, may or may not have been observed in total absence of moisture. This is another reason to examine transition-region systems more thoroughly than heretofore.

Amongst possible solid systems one could suggest that the proton conductor based on hydrated uranyl and phosphorus oxides

might be considered as a transition-region electrolyte. Preliminary work on the rechargeable cell



has been reported. Perhaps lighter hydrides will be found to be tame in this low-moisture electrolyte.

V. ELECTROCHEMICAL SPECTROSCOPY

New approaches are necessary if better understanding of the processes, better quality control during manufacture, and better operational control of the power source, are to be achieved. Three examples have been chosen to illustrate kinds of new information on aqueous systems which we think to be important.

(1) The first has to do with reactions which take place at the surfaces of anodically formed (hydr)oxides, during overcharge, in alkali batteries. (2) The second bears on the effects of organic degradation-products on passivation. (3) The third is concerned with the refractory materials which accumulate on acidic fuel-cell catalysts after extended use. The techniques being used are electrochemical and spectroscopic. Elaboration on each of these topics follows a remark on limitations of present methods.

Electrochemical techniques (charging curves, multi-pulse potentiodynamic traces, cyclic voltammetry, etc.) although useful and provocative, are not sufficiently definitive to permit unique interpretation, or even description, of what is going on at the molecular level. Simultaneous identification of the reacting species in situ is necessary. Other than by fast spectroscopic means, such identification is next to impossible to achieve (See Fleischmann, ECS Extended Abstracts 76-1, 1976). Although the information so obtained may be only fragmentary, and is seldom unequivocal on identification, it does help provide a fresh view of the molecular mechanisms which can help us get better performance out of the system, be it higher energy density, greater longevity, etc. Although these techniques can be usefully applied to non-aqueous molten salt and solid electrolyte systems, their application to aqueous systems offers many surprises too. Almost every proposed mechanism of anodic oxidation or cathodic reduction includes free radicals as intermediates, and although the inferential evidence from rate theory and V/I curves, from cyclic voltammetry, from MPPD (multi-pulse potentiodynamic techniques), from photoelectron current transients, and other techniques, is quietly convincing, the skeptic longs for direct evidence, obtained directly from the operating cell itself. Some notes on three techniques in use at DREO are now offered.

Absorbed Species on Reactive Surfaces

The electrical performance of the Ni-Cd battery at normal and low temperature is affected in perplexing ways by what is on the reacting surfaces, both positive and negative. Hydroxycarbonates, polycarbonates, partially decomposed organic polymers and wetting agent, oxides and hydrated oxides, hydroxides and metallic species: all have been implicated as potential players in the overall processes which occur during charging and discharging of the battery. Verville is using fast-fourier-transform (FFT) analysis of repetitive infrared (IR) scans to separate out weak absorption signals by surface species from the background absorption noise of the battery plate -- with some success. The technique is elegant, but the specimen to be examined has to be dried well enough that OH bands from moisture do not bury the signal.

Studies on positive and negative plates of new and used Ni-Cds, and on specially prepared surfaces on nickel foils, have shown (6) that: (a) The surface material does indeed vary in composition over the surfaces; (b) Some effects previously ascribed to carbonates could come from hydr(oxides) only; (c) Carbonates do appear, and are indeed hard to remove; (d) Partially decomposed polymers from the separator or wetting agents can affect the behaviour of the nickel and the cadmium electrodes during the cycling operation of the battery; (e) Very careful specification and selection of the separator material and wetting agent can lead to cells of superior performance, whether in aircraft batteries (6b) or satellite batteries (6c).

In recent work, the electrophoretic deposition of active material into sintered nickel plaques has been shown to be markedly sensitive to the initial wettability of the plaque and dependent upon the organic materials which are adsorbed upon them during the deposition (6b). The identification of the controlling species is as yet incomplete.

The FFTIR reflectance technique may yet prove insufficiently discriminative, but at this stage it does appear that some real further progress is being made in identifying the materials responsible for the variable cranking performance and rechargeability of the Ni-Cd battery at low temperatures. Should it not be applicable to Fe, LaNi_5H_x , Fe-Ti-H, and Zn electrodes also?

It is suggested that this FFT IR reflectance technique could be applied with enthusiasm to the other negative electrodes used in alkali batteries. We might be surprised at what the organic decomposition products are affecting the limiting performance parameters which were mentioned at the beginning.

Free-Radicals in Battery Electrolyte

If a free-radical exists in a solution even in minute quantities, it can sometimes be detected by its unique electron spin resonance (ESR) spectrum. Information on its presence in the electrochemical cell, and on its movement and fate, would be unique information: at least we would know for certain what one species is doing. Many studies of the traps, and of trapped species, in and on dry solids have appeared. Many radicals have been formed electrochemically, and have been detected and followed by ESR, most of them being organic free-radicals with lifetimes of minutes or more, in aqueous and/or in non-aqueous solutions. In a few cases the role of radicals trapped in micelle polymers has been surmised from ESR results. The simple inorganic free radicals have escaped detection. Or have they?

One such discovery was reported from our laboratory in 1971. The anodic formation of the free radical ions, ozonide (O_3^-) and its cousin superoxyl (O_2^-), in aqueous KOH, at low temperatures, was unpredicted in published oxygen evolution mechanisms. The details of the formation, of O_3^- and its stability, and on the likely nature of the surfaces suitable for its formation and release, and on other aspects, have been reported by Gardner et al. (7a). One of the most interesting findings was that O_3^- forms copiously from an overcharging silver oxide electrode but not at all from an overcharging nickel hydroxide electrode. Another curious finding was that either O_2^- or O_3^- can be ejected from the anodizing cadmium electrode by changing the KOH concentration and the temperature. The question arises: How are these surfaces so different one from the other? Or, why can (or must) one oxygen-bathed (hydr)oxide surface eject radicals while another cannot? Consider air-electrodes. One could imagine that adsorbed superoxyl radicals may well escape into the electrolyte from a silver-oxide catalyzed air electrode, or a manganese-catalyzed one. But do they?

Armstrong's (8) success in developing practical air electrodes which operate well at very low temperatures has, in our view, been a spectacular achievement. He uses "manganese oxide" catalysts and carefully controlled pore sizes. These, and Tseung's super-catalysts (JECS, 125, 1660 (1978)) based on doped perovskites, which seem to permit the direct 4-electron reduction of O_2 without the formation of adsorbed HO_2 (O_2^- in alkali), may or may not eject radicals into solution. Since O_2^- or O_3^- could end up biting holes in the separator, these are not idle questions.

It should be mentioned that most of the current experimental work in our laboratory using ESR is concerned with the cathodic reduction of SO_2 in NON-aqueous cells. SO_2^- and $S_2O_4^-$ have been distinguished and are being followed. In general, radicals are

stable longer in non-aqueous electrolytes, and the researcher is often richly and more quickly rewarded, without suffering the experimental hurdles of trying to detect and follow short-lived species in aqueous solution. Yet, the practical rewards may be greater from work on aqueous systems.

The main message is clear: there may well be other, highly reactive, free-radicals escaping, one way or another, into battery and fuel cell electrolytes, and it would be nice to know what they are, where they go and what they do. Perhaps they can be suppressed or controlled better, or even utilized in some ingenious way to improve the performance.

New Molecular Species

In acids things are different. Or are they? Direct and unequivocal detection of adsorbed species on surfaces is still not possible in situ, although equivocal information can be obtained by ellipsometry, by reflectance photometry, photo-stimulation and such techniques. Laser-Raman techniques for examining surface species show some real promise even though the process giving rise to the spectra is not yet well understood (Van Duyne, J. Phys., Colloq. 1977). Thus although the concentration of adsorbed species is very low for conventional Raman, the inadequate theoretical treatment for adsorbed species further militates against the quality of the spectrum from the positive identification of the "scattering species". But could adsorbed species not be used as a probe to study battery-active surfaces? Via laser Raman?

Laser-Raman spectra of species in solution seem to hold more promise for battery and fuel-cell researchers at this stage of development of the technique, and program of study of complexes is being pursued at DREO. Adams et al. (9a) have recently reported on a study of the condensation reactions and the hydrolysis of phosphoric acid as a function of concentration, temperature and pressure. The main result of direct interest to this Study Institute probably is the evidence for the existence of the dimer of phosphoric acid, in hot concentrated solution. It was proposed at an ECS meeting that some such species must sit on the supported platinum electrocatalyst in the phosphoric acid fuel cell, and do two things: (a) Block active sites on the Pt, and (b) Aid migration of the Pt, through the formation of some unknown solution-complex. Hence the hydrocarbon/air fuel-cell specialists probably are on the right track in their attempts to inhibit the formation of the dimer and defeat its effects. A spectroscopic (L-R) investigation directed towards the same goal, and the desirable improvement in performance, might be very rewarding.

A L-R study of the complexes of Br_2 in aqueous electrolytes of interest in the Zn/Br_2 storage battery system is also in progress (9b), but although the information being obtained on complexing is thought-provoking, it is premature yet to discuss its practicality.

One concludes that the L-R technique can give practical information on complexing in aqueous solutions, information which can be unequivocal and which cannot be obtained by IR because of masking by water bands, or by any other technique. It is one new tool which battery chemists could use more fruitfully.

VI. REMARKS ON TECHNIQUES & EXOTIC MATERIALS

Other Techniques

There are two main components to electrochemistry, the electrical part and the chemical part. To do research on one without correlating with the other seems fruitless. It makes for lots of papers but not much true understanding. Techniques for continuous measurement physical and chemical properties of the active materials at the solid/liquid interphase in situ are really still quite crude and uninformative. Three possibilities which seem worthy of further development:

(a) Continuous snapshot X-ray diffraction probably could be developed to be a much more useful tool. Painstaking work has already shown the power (and the limitations) of X-ray diffraction of working surfaces (Burbank, JECs, 117, 299 (1970), 118, 525 (1971)). The sensitivity of the detector is still too low for rapid scan, however, and therefore it is difficult to follow changes in the diffracting structure of the working active mass. One can take out and dry the sample, but as soon as the current is cut it probably changes. Snapshot capability for X-ray diffraction equipment needs to be developed.

(b) Quick-freezing of surfaces under working conditions, freeze-drying and subsequent analysis--whether by micro-chemistry, Auger or other methods which yield composition and ratios--should lead to a better correlation of compositional changes with electrical performance, and hence to better control procedures. We need to rekindle the patience and persistence of earlier researchers in the matter of painstaking preparation of samples for analysis.

(c) Differential scanning calorimetry (DSC) not only of active-mass materials but also of support materials in electrochemical cells could be used more extensively than it is,

now that the experimental tools and the theoretical background of thermal decomposition of solids are so much more readily available than they were a decade ago. Using the DSC, Nagy et al. (10) early recognized three states of AgO, and recommended the DSC fingerprint as a criterion for selection of AgO powders for reserve-primary torpedo batteries. Hydrides are another important class of materials of which the thermodynamic and kinetics of charge and discharge of hydrogen stored could be so fruitfully and quickly scanned by DSC and the metallurgical preparative procedures of the useful ternary and quaternary alloys usefully optimized.

Exploratory Materials

In the sense that so little definitive and unequivocal information is known about the composition and behavior of the active masses of electrochemical cells during the operation, it could be argued that all active masses are "exotic" materials. In this paper we have concentrated on ways of learning more about these active components of aqueous cells. The theme is that, if we know how they work and what can go wrong, we should be able to modify their composition or structure and obtain improved performance.

Little has been said about side reactions which can undermine the supporting structure of the active material, either chemically or physically, or about corrosion reactions of the container or other components of the cell. By contrast with what happens in non-aqueous and molten-salt cells, in aqueous cells usually some well-known material can be selected which will not undergo destructive side reactions and it is the performance of the active masses which limits the performance of the cell. Hence, major improvements in the aqueous cell systems can be expected only from major improvements in the performance of the active masses: whether by doping, by changing the support structure or using different supporting materials, or by decreasing the amount of electrolyte or non-active components.

However, occasionally a new material is developed which meets the stiff criteria for use in electrochemical cells, and permits an advanced battery to be conceived. The term "exotic", literally "foreign", carries the further inference, "expensive". Advanced batteries can sometimes be made, at higher expense, using exotic materials, which employ conventional aqueous couples. There are two classes.

The first class contains those materials which have been developed to improve the conventional systems. Examples? (i) The radiation-grafted copolymers prepared as battery separators for the Zn-Ag system is an example. With it, this high-energy-

density, high-power-density system is rechargeable for a hundred cycles, without it, maybe five. The material was developed to meet a need: if it could be done, then the system would be cyclable. (ii) Polypropylene fibre mat'es (first) and then porous sheets (later) were developed to improve the longevity and the high-temperature stability of Ni-Cd satellite and aircraft batteries. (iii) The lead-calcium (-plus) alloys used as grid material in the lead-acid system, and the spirally-wound internal designs, were developed to make possible the low-maintenance and sealed lead-acid batteries which are now common. (iv) Lead chloride (cheap) was developed into suitable plate material to replace the strategic and expensive silver chloride in sonobuoys. (v) The lanthanum-nickel cobaltate electrocatalysts have been developed to permit the four-electron (more highly energetic) reduction of oxygen in the air electrode of air batteries and fuel-cells, and for energetically more efficient electrolyzers. (vi) The advent of the hydrides for storage of the fuel, and in thermal management during operation. These are but some examples of the development of materials which are incorporated into (yesterday's?) conventional batteries for the purpose of offering us advanced systems.

The second class contains materials which have been developed for other purposes but which may enable us to conceive and build an advanced battery from standard aqueous systems. Amongst these support materials we list generally the following: (a) AlN and SiC and BN; (b) glasses and ceramics based on silicates and oxides; (c) polyphenylene sulfide, or oxide, and polyethersulfone; (d) vitreous carbon-fibre felt and non-conducting carbon fibre paper. It is a sad but necessary comment that it is typical that the impurity content and even the stoichiometry of these materials is usually very poorly known to the user, and that, as a result, he finds that the performance in his particular environment will vary from batch to batch. I have been impressed with attention to stoichiometry and impurity data recently published on SiC. We need more such chemical and physical characterization. But these are support materials.

From a big list of new active materials one is intrigued by new solid-ion conductors. Consider only two: (a) Nazirpsio, a solid ionic conductor based on the mixed silicates and phosphates of sodium and zirconium, and (b) NaI-doped polyethylene oxide. Both are sodium-ion conductors. Both have potential as candidate materials for separators (completely anhydrous?) or as solid electrolytes (transition region type?). Some of our views on these (5a), as well as on the use of some of the new alloys of titanium (11) in batteries have been published elsewhere. It is too bad that so little information on measurements of corrosion resistance, of elasticity and related mechanical properties, and of fracture mechanics can be found in the literature on materials

such as BN, SiC and glassy carbon, since the performance in cells must be intimately related to the microcrystalline structure and to the exact composition of the material. Finally, one can also become intrigued with the nitrides of sulfur. One could surmise that the metallic ringed compound S_4N_4 is an electrocatalyst, and one day will show properties as interesting to fuel-cell chemists as the dichalcogenides are showing to battery chemists.

EPILOGUE

"The scientific barriers to be overcome in advancing defense, energy, communication and production material technologies are all materials related. Similarly the engineering barriers to be overcome in obtaining increased efficiency, simplicity and reliability in systems technologies are all design related.

To attain both the cost and the confidence levels required for timely utilization -- insight not research, leadership not management, innovations not ideas, and accomplishments not theories must be stressed.

The risk is competitive obsolescence, whether measured as corporate profits, national efficiency or technology leadership. The needs....for the foreseeable future will be materials limited".

W.L. Lachman (1979)

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REFLECTION ON SOME RECENT STUDIES OF IMPORTANCE
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