KINETIC BARRIERS TO THE PREFERRED ELECTRODE PROCESS IN SUBZERO BATTERY ELECTROLYTES*

E. J. CASEY

Defence Research Establishment Ottawa, Ottawa K1A 0Z4, Ontario (Canada)

Summary

The factors which limit the rate and completeness of the charge and discharge processes of battery systems at low temperatures are discussed: low concentration of reactants, low fluidity and relaxation rate of electrolyte, low nucleation and growth rate of reaction products, low ionic- *vs.* semiconductivity of reaction products, and low average pore size in the plates.

Systems based on water, ammonia and aprotic solvents were reviewed. For the better −40 °C performers an attempt is made to identify the most important kinetic barrier to improved electrochemical performance of the system.

It is noted that definitive experimental information at −40 °C is still scarce.

General reflections on slow steps at −40 °C

Since this battery laboratory was established in 1950 some one of the researchers has always seemed to be intrigued by electrochemical processes at low temperatures. The common goal has been to identify the slow steps and to take remedial action. Aqueous-, organic-, and ammonia-based electrolyte systems have all been of interest at one time or other. It is probably fair to claim that the selection, care, and use of batteries at low temperatures by our colleagues within the military and civilian communities — particularly for search and rescue equipment, aeroplanes and vehicles — has benefitted from this continued interest in low-temperature phenomena at DREO. It has also provided a line of research which is not only germane to the Canadian scene, but is both interesting and demanding.

Things are different at low temperatures, principally because steps along the reaction path, which are fast enough to be unobtrusive at normal temperatures, can often become of prime importance (essentially frozen out) as the temperature is lowered. If each consecutive or parallel step has a temperature coefficient of rate which is even slightly different from that of all the other steps in the overall process, then one cannot but expect that the rate-determining step (that is, the overpotential-determining step) will change as

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the temperature is lowered. All steps are slower, of course. One can recall the kineticist's rough rule-of-thumb: between +20 °C and −40 °C the rates for mass-transfer processes will be 7 to 10 times slower, and for activation-controlled processes will be 12 to 20 times slower, if indeed they are not frozen out altogether (100 times slower, say).

In preparing this paper it was decided to focus attention on battery processes which *do* occur at −40 °C, albeit slowly, and to see if there are any new improvements or directions for investigation which might be suggested from a synthesis of the new information to be offered and that already available in the literature.

Fluid and conductive electrolytes are critical to battery operation at −40 °C. So also are the conductive properties of solid films formed *in situ* over the redox materials of the active masses. From a consideration of these, and the accessibility of reactants to each other, one can begin to identify the kinetic barriers to the preferred electrode process at −40 °C, and take steps either to circumvent or to catalyze the offending slow steps.

Critical properties of electrolytes for good −40 °C performance

In Table 1 are listed some electrolytes in which electrochemical reactions can proceed at a practical and useful rate in battery systems at −40 °C. Data given were selected from refs. 1 - 6.

Selection rules for this short list are very stringent. The electrolyte must provide reactants and it must remove products. It must remain fluid enough to mix easily and to maintain homogeneous composition. It must distribute the heat which is produced by the inevitable inhomogeneities over the reacting surfaces and thereby prevent hot spots (or frozen spots) from appearing. It must remain ionically conductive. It must not accumulate shuttle-operative redox species or free radicals which can provide the equivalent of electronic short circuits. It must remain stable to anodic oxidation and cathodic reduction within practical limits of potential.

Note, firstly, that each of these proven candidates in Table 1 is a composite electrolyte: an electrolyte system composed of at least two components, but some with three or more. Note, secondly, that the range of composition which the electrolyte must conserve, without phase separation or freezing at −40 °C, is really quite narrow in each case; outside these limits a solid settles out.

Complex formation seems to play an essential role, whether it be a molecular association which lowers the vapor pressure of one of the components into manageable range, as is the case with methanol in ammonia and with sulfur dioxide in acetonitrile; or a charge-transfer complex, as in the case of sulfur trioxide in water or boron trifluoride in hydrogen fluoride. These complexes must be labile and they must be non-polymeric. Given a structure-breaking stimulus at the electrode, the distorted complex must be able to reform (relax) rapidly by reaction with neighboring reactant. Otherwise stated,

TABLE 1

Some battery electrolytes liquid at $-40\ ^\circ C$

Solvent	T_f ($^\circ$C)	Solute(s)	Optimum composition (Wt.%)	Liquid limits at $-40\ ^\circ$C
1. H_2O	0	H_2SO_4	39	30 - 46
		HBF_4	38	35 - 42
		KOH	31.5	28 - 35
		LiCl	22	19 - 31
2. NH_3	-78	CH_3OH; NH_4SCN	58; 17	broad; 5 - 20
3. CH_3CN	-46	SO_2; LiBr	70; 8	40 - 80, 3 - 10
4. $C_3H_6CO_3$	-49	KPF_6	10	6 - 12
5. $HCOOCH_3$	-99	$LiAsF_6$; $LiBF_4$	26; 6.5	15 - 30; 4 - 10

if the activation energies are not low and if mass transfer coefficients are not high at $-40\ ^\circ$C, the electrolyte itself may be responsible for the slow step: it may not be able to re-form fast enough from some structure-breaking step at the electrode, and an undesirable product may settle out.

With these limitations it is perhaps surprising that the list in Table 1 is as long as it is.

Performance of the better low-temperature battery systems

Which battery systems actually do deliver useful work at $-40\ ^\circ$C? Figure 1 (from [4]) shows several battery systems whose performances have been found practical. An oxyanion system, an organic electrolyte system and a liquid-ammonia-based system are included, along with some aqueous systems. Table 2 is an updated, selected list of systems for which useful $-40\ ^\circ$C output has been demonstrated. The performance of the Ni–Cd and Pb-acid systems at $-40\ ^\circ$C varies [5]. Other systems are less widely used and less well known [6 - 10]. A few examples follow. The performance of each of these systems at $-40\ ^\circ$C is impressive.

Figure 2 shows the discharge behavior of the Pb–PbO_2 system at $-40\ ^\circ$C in aqueous fluoboric acid [7]. The reaction product is soluble. The electrolyte responds quickly and dissolves the reaction products. The potential remains constant during discharge, at a very useful c.d.

Some aqueous salt systems have also been developed and described, and their $-40\ ^\circ$C performance given: Mg/MnO_2 [8a], Mg/AgCl [8b], Mg/air [8c].

Liquid-ammonia-based primary batteries have been developed and described [2]. Figure 3 shows discharge behavior of the zinc–metadinitrobenzene system at $-40\ ^\circ$C, at low c.d., in one liquid-ammonia-based electrolyte [9a]; Fig. 4 shows the performance of the Mg/$HgSO_4$ system at high c.d., in another [9b]. The Mg/S system also works well [9c].
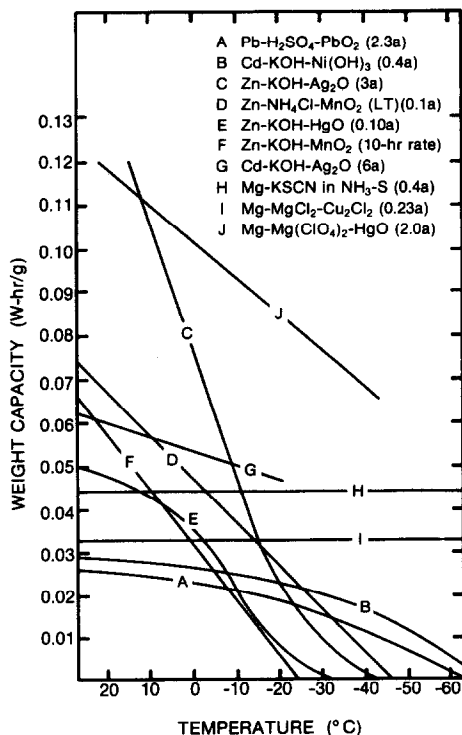
A Pb-H$_2$SO$_4$-PbO$_2$ (2.3a)
B Cd-KOH-Ni(OH)$_3$ (0.4a)
C Zn-KOH-Ag$_2$O (3a)
D Zn-NH$_4$Cl-MnO$_2$ (LT)(0.1a)
E Zn-KOH-HgO (0.10a)
F Zn-KOH-MnO$_2$ (10-hr rate)
G Cd-KOH-Ag$_2$O (6a)
H Mg-KSCN in NH$_3$-S (0.4a)
I Mg-MgCl$_2$-Cu$_2$Cl$_2$ (0.23a)
J Mg-Mg(ClO$_4$)$_2$-HgO (2.0a)

Fig. 1. Energy density as a function of temperature. Useful systems at −40 °C: A, B, H, I, J. From ref. 4.

TABLE 2

The better performers at − 40 °C*

Cd/KOH$_{aq}$/NiOOH			[4]
H$_2$/KOH$_{aq}$/NiOOH			[6]
Pb/H$_2$SO$_{4aq}$/PbO$_2$			[5]
Pb/HBF$_{4aq}$/PbO$_2$			[7]
Mg	Mg(ClO$_4$)$_{2aq}$	MnO$_2$	[8a]
	LiCl$_{aq}$	AgCl	[8b]
	MgCl$_{2aq}$	air	[8c]
Mg; Zn	Liq-NH$_3$	m-dnb	[9a]
	+	HgSO$_4$	[9b]
	salts	S	[9c]
Li	CH$_3$CN		
	+	SO$_2$	[10a - c]
	LiBr		

*The Cd, Pb and H$_2$ systems are rechargeable at −40 °C (although Pb only slowly and partially). The Mg, Zn and Li systems are primaries only, at this stage of development. In all cases, electrolyte concentrations must be kept within the limits shown in Table 1.
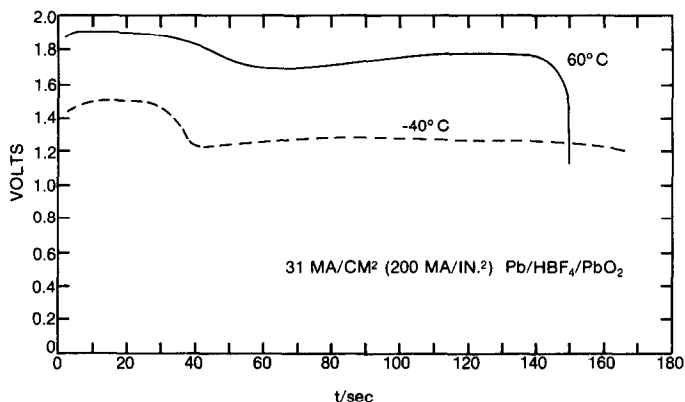
Fig. 2. Output (V vs. t) of an operational $Pb/HBF_4/PbO_2$ battery at -40 °C after rapid filling with low-viscosity electrolyte (38% HBF_4). From ref. 7.
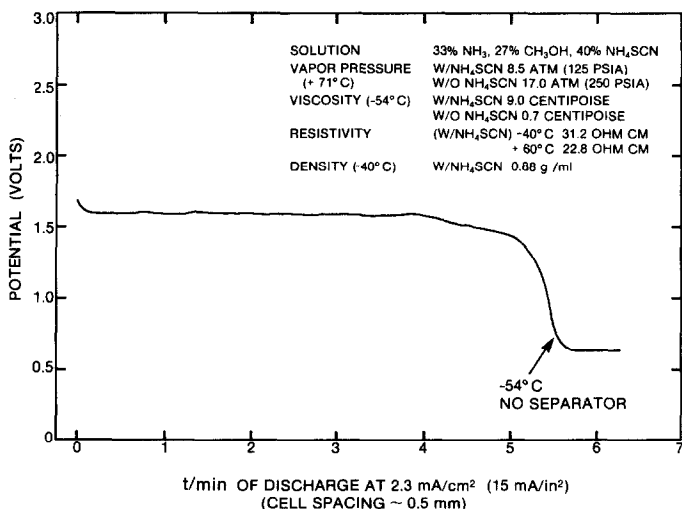

Fig. 3. Output (V vs. t) of a developmental $Zn/liq\text{-}NH_3/m\text{-}dnb$ battery at very low temperature. After ref. 9a. Note the low viscosity of the electrolyte at -54 °C, yet low vapor pressure at $+71$ °C.

Figure 5 demonstrates discharges of the reaction of Li with SO_2 in an acetonitrile-based electrolyte, at various temperatures including -40 °C. Data were taken on commercial cells and have been reported [10].

It can be concluded that useful work can indeed be realized from several redox systems at -40 °C, provided that care is taken with design of plates and cells and with the composition of the electrolyte. Higher energy density and recharge-ability should be achieved if effort were applied.

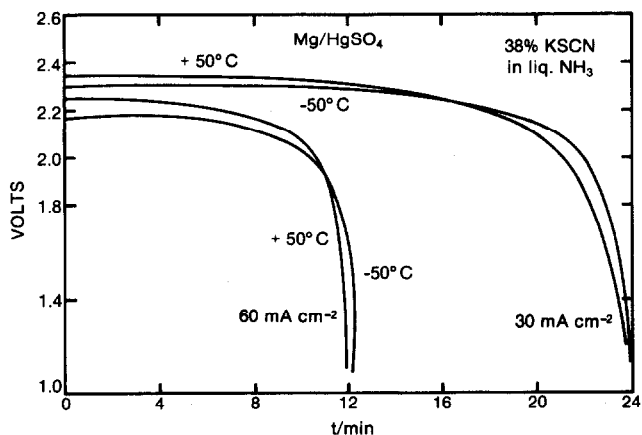The barriers to better performance at -40 °C will now be considered.

Fig. 4. Impressive performance of the Mg/liq NH_3/$HgSO_4$ battery at -50 °C, compared with that at +50 °C, at a very practical current density [2, 9b].
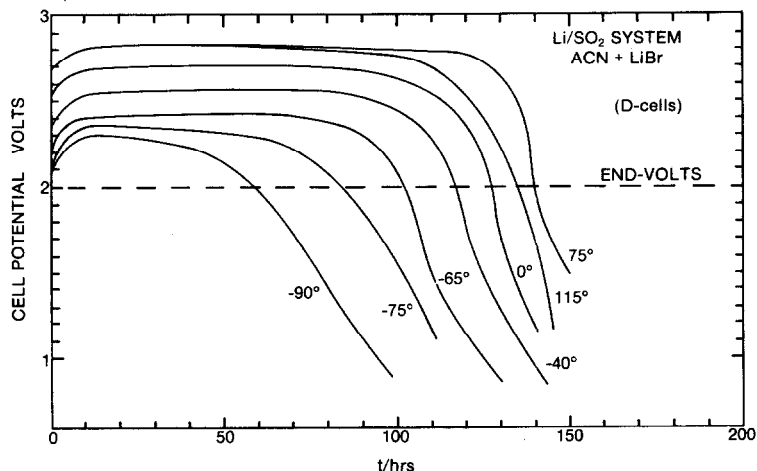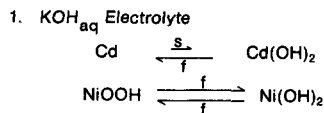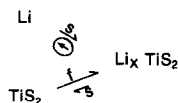

Fig. 5. Low-temperature (°F) output of well-made lithium–SO_2 cells. From ref. 10b.

Some blocked or hindered redox steps in the better systems

Each of the systems below H_2SO_4 in Table 2 is a primary system, not rechargeable. In other words, at least one of the four redox processes necessary for rechargeability is blocked (Fig. 6). Many half-cells are not reversible in the practical sense, certainly not at a useful rate at -40 °C; the kinetic barrier in one direction, whatever its nature, is usually much higher than in the other. For example, the barrier to recharge to Zn or S may be in some step in the mass-transfer or complex-reorientation of zinc or sulfide ions from the bulk solution. Barriers to recharging of Li at normal temperatures have been identified and discussed [11], but no studies done at $-40°$ have been reported.

1. KOH$_{aq}$ Electrolyte

$$Cd \underset{f}{\overset{s}{\longleftarrow}} Cd(OH)_2$$

$$NiOOH \underset{f}{\overset{f}{\rightleftharpoons}} Ni(OH)_2$$

2. MF + LiAsF$_6$ Electrolyte

$$Li \quad Li_x TiS_2$$
$$TiS_2$$

3. NH$_3$ + CH$_3$OH + KSCN Electrolyte

$$Zn \underset{\ominus}{\overset{f}{\longrightarrow}} Zn^{++} \text{ prods.}$$

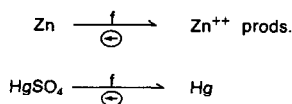$$HgSO_4 \underset{\ominus}{\overset{f}{\longrightarrow}} Hg$$

Fig. 6. Schematic representation of some slow(s), fast(f), blocked $\ominus$ processes at -40 °C, length of arrow indicating relative speed.

In the Cd/KOHaq/NiOOH system all four (Fig. 6) redox processes can, and do, occur at reasonable rates at -40 °C, provided that [4, 12, 13] : (a) the electrolyte is maintained at, or slightly above, the eutectic composition of 31.5% KOH and contains less than 4.5% carbonate; (b) the electrodes are designed so that rapid accessibility of the electrolyte to the Cd/Cd(OH)$_2$ and NiOOH/Ni(OH)$_2$ electrodes is assured. The cadmium electrode can be charged rapidly (solid-state mechanism?), but it will rapidly polarize and be blocked if allowed to be oxidized (discharged) at -40 °C at a rate much above 0.1 A cm^{-2} of plate area, (it is thought because the under-layer of primary reaction product, "CdO", becomes semiconducting instead of ion-conducting at a small but critical thickness).

By contrast, it is surmised that nickel hydroxide is so effective at -40 °C because it is already a layered compound, whose layers simply expand during charge to accomodate the insertion of oxygen atoms without further need for nucleation and/or growth. If this is so, by analogy one might expect that the dichalcogenide family may present a suitable candidate with the same properties in aprotic solvents.

One might conclude at this stage that if slow (or zero) nucleation-rate is the critical barrier to charge acceptance of other (hydro)oxide systems at -40 °C, such as Pb/"PbO$_2$" or Ag/"Ag$_2$O$_3$", the search should turn towards mixed compounds which can form expansive lattices without further nucleation at -40 °C. In other words, doping of electrodes or electrolytes by cations or anions, respectively, might become a fruitful line of investigation: mixed oxy-sulfides and mixed oxy-halides suggest themselves. Metal alloys with expanders suggest themselves for negative plates, for the same reason.
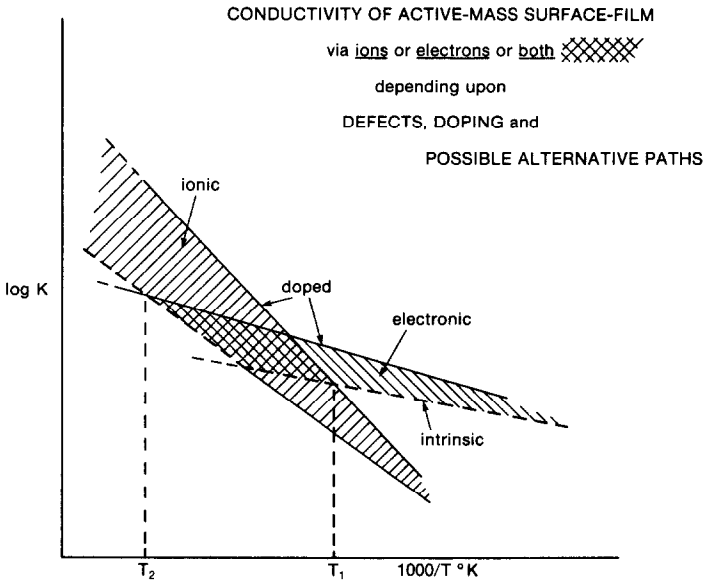
Fig. 7. Schematic plot of log conductivity *vs.* inverse temperature for a thin semi- or ion-conducting surface film. Description and implications in text.

Critical properties of thin surface films at −40 °C

Charge can usually pass through a solid film in more than one way, depending upon composition, contacts, and temperature [14]. If the surface film which grows during charge or discharge becomes continuous and covers the whole active mass, semi-*vs.*-ion-conductivity can become critical to the progress of the process.

In the first case, material is precipitated into or infused into the active mass through some sort of ionic movement. In the second case, the material remains invariant while electrons or holes carry charge through the mass. There is much indirect evidence that many surface films can act as either ionic or electronic conductors under different experimental conditions, sometimes both in parallel. This is illustrated schematically in Fig. 7.

The envelope indicates the effects of variable composition. Note that, depending upon composition, a temperature range exists over which the solid may act either as a semiconductor or as an electrolytic conductor, or both. Generally, ionic conductivity becomes lower than semiconductivity at low temperatures. As a result, the reaction which prevails may change as temperature is lowered, from one which works the active mass to one in which the active mass is by-passed — from a charge-storage (or charge-delivery) reaction to an alternative, such as a wasteful gas evolution. When ions and electrons can both move at the same field strength through a surface film, the one which actually occurs will depend upon the nature of the available surface states.
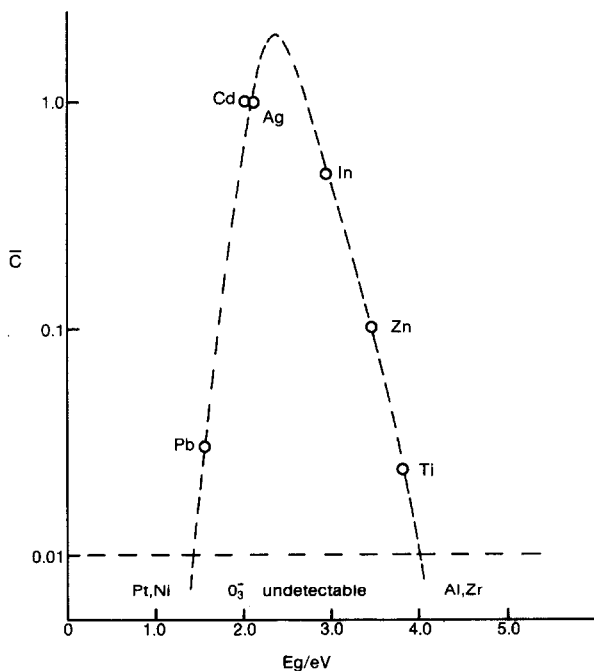
Fig. 8. Concentration (normalized) of ozonide free-radical ion O_3^- accumulated at steady state in anolyte (30% KOHaq) during anodic oxygen evolution at low temperature for different metals. After ref. 17 b.

In an earlier paper on anodic oxidation of silver to Ag_2O, AgO, and "Ag_2O_3" at -40 °C, we gave evidence that a blanket of oxygen-containing species covers the surface if the electrode is in the steady state at potentials above the oxygen evolution potential, and that only a small amount of either AgO or "Ag_2O_3" (but not both) accumulates in the surface film in the process [15]. The steady state condition is characterized by a thin film of higher oxide which has stopped growing, perhaps due to, or resulting in, the formation of molecular fragments adsorbed on the surface sites. Recent work on the anodic oxidation of Pb in H_2SO_4 at -40 °C in this Laboratory reveals the same general behavior [16 a - c]. Catalysis of the $PbSO_4 \rightarrow PbO_2$ conversion at -40 °C by doping and other means has not been systematically investigated so far.

Slow ionic movement through the surface film, slow nucleation and/or growth, and slow dissolution and precipitation: all are eminently qualified candidates for the undesirable behavior award. Unfortunately, they seem to be experimentally indistinguishable, or even characterizable, at -40 °C by the known electrochemical techniques.

In the next section of this paper some recent work on four particular topics of continued practical interest is noted, two on aqueous and two on non-aqueous electrolytes.

Some recent experimental work at −40 °C

(a) KOH_{aq}

The blanket effect of oxygen-containing species adsorbed on the surface of several "oxided" metals during oxygen evolution was examined [17] by following the buildup of O_3^- radical-ions in the anolyte at −40 °C. A systematic relation between amount of accumulated O_3^- and the reported work-function of the compositional oxide presumed to be formed anodically at −20 °C was reported [17b], and extended (Fig. 8). The fact that from oxided metals such as Ni (Co? Fe?) no detectable O_3^- is anodically ejected into the electrolyte suggests that the peroxide link —O—O— is not formed on the surfaces: instead, with oxided Ni the (oxidizing) process continues to take place by the continued insertion of O or O^- into the lattice to form phase-oxide. (On oxided Pt the oxygen gas is formed from O_{ads}.) The practical problem can now be simply stated: if one can find a way to inhibit the formation of the peroxide linkage, perhaps phase-oxide will continue to grow, and not stop.

(b) H_2SO_{4aq}

Both solid-state and solution–precipitation barriers have been blamed by different investigators [4, 16, 18, 19] for the failure of the $PbSO_4/PbO_2$ electrode to accept charge rapidly, or in quantity, at −40 °C. The most seriously measured experimental number analyzed and interpreted in recent years which bears on this problem is the activation energy for the transformation at −40 °C; it varies from 18 to 32 kcal/mole; but one can readily argue that even this number cannot be used to distinguish unequivocally a solid-state from a solution–precipitation mechanism. Further, the stability and low solubility of the tetravalent lead sulfate, $Pb(SO_4)_2$, in oleum at room temperature [20], and the oleum-like properties of eutectic $H_2SO_4–H_2O$ at −40 °C — as well as alternative reaction products based on the high oxides of sulfur, viz., $Pb(S_2O_8)_2$ and $Pb(SO_5)_2$ — make an unequivocal barrier-assignment impossible at this stage.

Too high an applied potential — if one attempts to force ionic conductivity and oxidation of $PbSO_4$ to PbO_2 — can be disadvantageous. One recent finding about the role which H_2O_2 can play, if it exists or is formed in H_2SO_4 electrolyte at −40 °C is illustrated in Fig. 9, which gives evidence that hydrogen peroxide causes the destruction (reduction) of the higher phase-oxide at −40 °C, and also prevents its anodic formation by providing a by-pass mechanism for the anodic evolution of oxygen. Again it appears that the —O—O— linkage thwarts the progress of the preferred electrode reaction. The role which perchlorate [20b] and other anions might play at −40 °C would seem to be well worth investigating.

(c) Liq-NH_3

The cold-weather potential of liquid-ammonia-based electrolytes was one of the first interests of this Laboratory [21], but the high vapor pressure
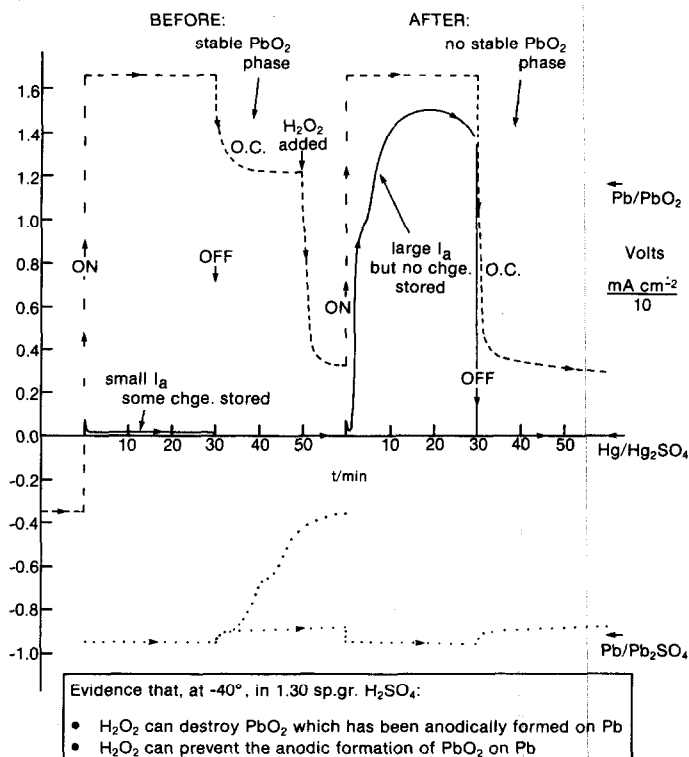
Fig. 9. Typical chronological traces of potential and current during attempts to isolate the role of peroxide on the formation and stability of "PbO$_2$" on a sulfated pure lead (5 nines) surface at −40 °C. Periods of anodic polarization followed by periods of potential decay.

and electronic conductivity were thought to be too troublesome. Interest reawakened because of marked successes elsewhere in vapor-pressure reduction and gettering of electrons, and the development of practical reserve-primary low-temperature batteries in the 1960s [2, 9]. Improved techniques for handling alkali metals, and the recent work of Schindewolf and others [22] on metal- and anion-complexing in metal-winning liq-NH$_3$ electrolytes suggest that a new look be taken at rechargeable battery systems based on liq-NH$_3$ or the liquid amides. These electrolytes are remarkable for their very high fluidity and conductivity at −40 °C and even lower temperatures.

(d) S- and N-Electrolytes

Although many organic and inorganic solvents are liquid at −40 °C, few form electrolytes with sufficient conductivity to be useful at low temperatures. Several SO$_2$ systems are currently under investigation by others in this Laboratory [23a], and MF systems have been studied in collaborative work elsewhere [3]. No work has so far been reported on any low-temperature organic system capable of recharge at −40 °C. As noted (Fig. 6), the

TABLE 3

Barrier assignments in some practical systems at $-40\ ^\circ C$

System	Slow step	Barrier
Cd/KOHaq/NiOOH	Cd oxidn.	CdO conductivity
Pb/H_2SO_4aq/PbO_2	$PbSO_4$ to PbO_2	PbO_2 nucleation; H_2SO_4 relax.
Zn/NH_4SCN; NH_3/S	S^{-x} to S; Zn^{2+} to Zn	crystal rearrangement
Li/LiBr; ACN/SO_2	Li^+ redn.	solub. of Li^+; LiBr cond.

real barriers will arise at the negative plate. Although Li and Na remain the metals of desire, they may not prove to be the metals of choice. Sulfur and the dichalcogenides seem to remain the cathode materials of promise. Low-temperature molten salts continue to offer surprise prospects as electrolytes, even "down to below dry-ice slush temperatures" [23b]. Recently [23c] certain mixtures of ringed N-halides with $AlCl_3$ have been shown to remain fluid to temperatures well below -40°.

General

Table 3 indicates four problem areas thought to warrant detailed kinetic study because of the seriousness of the problem and the prospects that major improvements can be expected to be made from the new informa-tion. That these cannot at the present time be stated in quantitative kinetic terms simply indicates the rather cursory investigations so far done at $-40\ ^\circ C$.

Since nucleation and conduction mechanisms may play such important roles at $-40\ ^\circ C$, and since the diagnostic techniques available for investigation of these phenomena at $-40\ ^\circ C$ are so limited, this author is hopeful [24] that new investigations of photo-effects on Cd, Pb, Li and other electrode processes at $-40\ ^\circ C$ will lead to a more complete understanding of the kinetic barriers. Pavlov's observations of photo-effects on the Pb electrode in $H_2SO_{4_{aq}}$ [19a], and the confirmatory work [19b] may have opened a new era. It is prudent to remember, however, that even *nucleation*, if slow, can be photo-stimulated [14], and must be considered along with *conduction* as a possible barrier process whenever photo-effects are observed at low temper-atures.

Porosity and accessibility of electrolyte to the active mass

None of the barriers discussed so far will be influential if electrolyte cannot present itself rapidly to the reaction interface. Channels must exist into the electrode of such dimensions that a viscous fluid can readily cir-culate and diffuse. Accessibility of electrolyte is supersensitive to structure at $-40\ ^\circ C$. Mass-transfer in the electrolyte will be the rate-limiting step if the dimensions of the channels are wrong: too long and too narrow. The impor-tance of this fact has been re-emphasized recently by Mrha *et al.* [25].
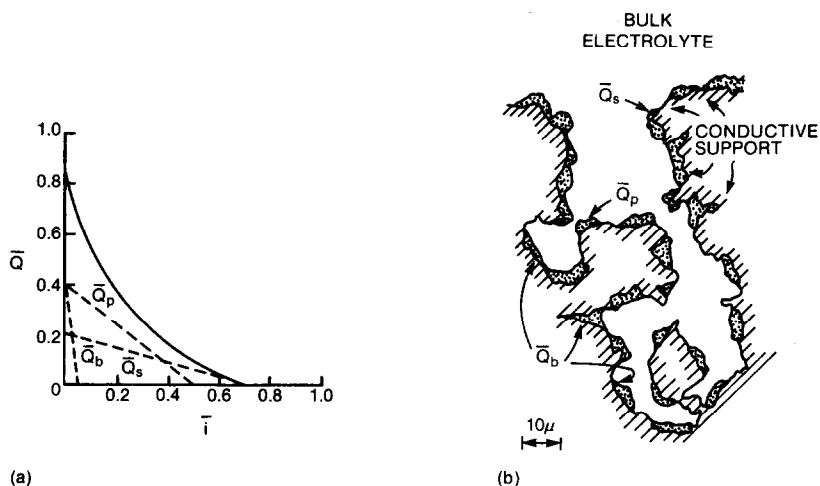
Fig. 10. Surface charge $\bar{Q}_s$ illustrated for evaluation of "choking index", $1 - \bar{Q}_s/\bar{Q}$.

In our experience plates must be $> 60\%$ channels for even a highly fluid electrolyte at -40 °C, if more than only the surface-exposed active material is to be able to react. Since V/I and Q/I data [2] are the sole experimental diagnostics known, some simple "choking index" [13] (see Fig. 10) has to be accepted as a basis for the design of plates intended for reaction at reasonable rates at -40 °C. (Elegant theoretical treatments of this problem are available as well [26].) The practical reality of preparing plates which are not only electrochemically active at useful rates, but which also retain physical and mechanical integrity during use, militates against porosities greater than about 75% — except perhaps in the case of the air electrode, in which no active material has to be retained [8c].

Only if suitable accessibility of conductive electrolyte can be achieved, can one's attention be unambiguously turned on barrier problems such as those listed in Table 3. This prerequisite is important.

Conclusions

(1) At -40 °C all steps in an electrochemical process are many times (7 - 100) slower than at $+20$ °C. Usually one step is frozen out first and becomes rate determining.

(2) The Ni–Cd system is the most versatile performer at -40 °C, if properly designed and maintained with regard to electrolyte composition and plate porosity. Both redox half-reactions are relatively rapidly reversible. The system is cyclable at practical rates. The (similar) Ni–H$_2$ system also shows great promise.

(3) The practical importance of identifying and circumventing the slow or blocking mechanism in the lead—acid system at −40 °C is recalled. The rate of recharge at the positive plate is slow and incomplete at −40 °C.

(4) The other −40 °C battery systems at this stage of their development must still be considered as primaries: not rechargeable yet at useful rates at −40 °C.

(5) Kinetic barriers to high-intrinsic-rate processes in the better low-temperature performers can be due to:

(a) low concentration of reactants;
(b) low fluidity and relaxation-rate of electrolyte;
(c) low nucleation- and/or growth-rate of reaction products;
(d) low ionic- *vs.* semi-conductivity of reaction products;
(e) low average pore-size within electrodes.

Although barrier assignments and mechanistic descriptions most often are equivocal and at best tentative, some assignments are offered and directions for further concentration of effort are suggested.

(6) New information on the role of surface-adsorbed intermediates which persist on the surface in aqueous electrolytes at −40 °C and which may inhibit or blanket the preferred electrode process (or catalyze alternative processes), is presented. Special concern derives from species containing the peroxide link.

Acknowledgements

References

1a G. J. Janz and R. P. T. Tomkins, *Nonaqueous Electrolytes Handbook*, Academic Press, New York, 1972.
 b T. C. Waddington, *Non Aqueous Electrolytes*, Academic Press, New York, 1965.
2   J. M. Freund and W. C. Spindler, Low Temperature Nonaqueous Cells, in G. W. Heise and N. C. Cahoon (eds.), *The Primary Battery I*, Wiley, New York, 1971.
3   H. J. Davis, Development of nonaqueous battery system, Noranda Research Center, *Canada DSS 13SR 3236019*, March, 1978.
4   Books on Batteries by: H. Bode, M. Barak; U. Falk and A. J. Salkind, R. Jasinski, A. Fleischer and J. J. Lander; Vinal, etc.
5   D. H. Collins (ed.), Batteries and Power Sources Series, *Proc. Biennial Int. Symp. on Power Sources, 1960 - 1978*.

6   T. L. Markin, R. Bennett, N. J. Bridger and R. M. Dell, in J. Thompson (ed.), *Power Sources 8*, Academic Press, Toronto, 1981, pp. 445 - 457.

7   M. A. Barron, *Proc. 23rd. Power Sources Conf., 1969*, PSC Publ. Cttee., US Army Electronics Command, Fort Monmouth, NJ, pp. 134 - 136.

8a   E. B. Cupp, *Proc. 23rd. Power Sources Conf., 1969*, PSC Publ. Cttee., US Army Electronics Command, Fort Monmouth, NJ, pp. 90 - 92.

 b   T. E. King and W. J. Moroz, *DRCL Tech. Notes Nos. 63 - 10; 75 - 13;* Defence Research Establishment Ottawa, Canada.

 c   W. A. Armstrong, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, 1975, p. 393.

9a   R. H. Comyn, J. T. Nelson, D. F. McMillen and W. H. Steuernagel, *Proc. 23rd. Power Sources Conf., 1969*, PSC Publ. Cttee., US Army Electronics Command, Fort Monmouth, NJ, pp. 134 - 136.

 b   O. Adlhart, *Proc. 14th Power Sources Conf., 1960*, PSC Publ. Cttee., US Army Electronics Command, Fort Monmouth, NJ, pp. 111 - 113.

 c   L. J. Minick, *Proc. 14th Power Sources Conf., 1960*, PSC Publ. Cttee., US Army Electronics Command, Fort Monmouth, NJ, pp. 114 - 116.

10a D. C. Linden, *J. Power Sources, 5* (1980) 208.

 b   W. J. Moroz, *DREO Reps. Nos. 74-1,* 1974; *81-11,* 1981.

11   S. B. Brummer, V. R. Koch and R. D. Rauh, in D. W. Murphy, J. Broadhead and B. C. E. Steele (eds. for NATO), *Materials for Advanced Batteries,* Plenum Press, New York, 1980.

12   E. J. Casey, *Proc. 1st Int. Battery Symp., SRDE Christchurch, UK, DRCL Rep. 219,* Defence Research Establishment Ottawa, Canada, 1958.

13   E. J. Casey and J. B. Vergette, *Electrochim. Acta, 14* (1968) 897.

14   T. J. Gray and V. D. Frechette, *Kinetics of Reactions in Ionic Systems,* Ch. 7 and 8, Plenum Press, 1969.

15a E. J. Casey and W. J. Moroz, *Can. J. Chem., 43* (1965) 1199.

 b   E. J. Casey and C. L. Gardner, *J. Electrochem. Soc., 122* (1975) 851.

16a E. M. L. Valeriote and L. D. Gallop, *J. Electrochem. Soc., 124* (1977) 380; E. Valeriote *et al.,* in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, p. 69; *Can J. Chem., 57* (1979) 974; *DREO Repts. 753,* Feb. 1977; *777,* June 1978.

 b   C. L. Gardner and F. Rocheleau, *DREO Tech. Note 75-1,* March 1975; L. Brossard and L. D. Gallop, *DREO Tech. Notes 79-15; 79-30.*

 c   M. M. Wright, COMINCO Ltd., and K.V.N. Rao, Gould Canada Ltd., personal communications and contract reports.

17a C. L. Gardner and E. J. Casey, *Can. J. Chem., 52* (1974) 930.

 b   E. J. Casey and C. L. Gardner, *Extended Abstr. of the Electrochem. Soc., Vol. 75-1,* May 1976, p. 147.

18   P. Ruetschi, Review on the lead–acid battery science and technology, *J. Power Sources, 2* (1978) 3.

19a C. Pavlov, S. Zanova and G. Papazov, *J. Electrochem. Soc., 124* (1977) 1522; D. Pavlov, *J. Electroanal. Chem., 118* (1981) 167.

 b   R. G. Barradas, A. Contractor, D. Nadezhin and D. Williams, *J. Electroanal. Chem.,* in press.

20a R. J. Gillespie and E. A. Robinson, Sulphuric Acid, Ch. 4, in T. C. Waddington (ed.), *Non Aqueous Electrolytes,* Academic Press, New York, 1965.

 b   C. Lazarides, N. A. Hampson and M. Henderson, *J. Appl. Electrochem., 11* (1981) 605.

21   J. W. Hodgins and E. A. Flood, *Can. J. Chem., 27B* (1949) 847, 861.

22a U. Schindewolf, *Pure Appl. Chem., 53* (1981) 1329.

 b   J. S. Gill, a review, *Pure Appl. Chem., 53* (1981) 1365.

23a K. C. Lee, W. A. Adams, C. L. Gardner, D. T. Fouchard and G. J. Donaldson, *Extended Abstr. of the Electrochem. Soc., Vol. 81-1,* 1981, p. 899; C. L. Gardner, D. T. Fouchard and W. R. Fawcett, *J. Electrochem. Soc., 128* (1981) 2345.

   b L. A. Kelly, personal communication; see C. P. Keszthelyi, *Electrochim. Acta.*, *26* (1981) 1261.

24   E. J. Casey, in D. W. Murphy, J. Broadhead and B. C. E. Steele (eds. for NATO), *Materials for Advanced Batteries*, Plenum Press, New York, 1980, p. 34.

25   J. Mrha and J. Jindra, *J. Power Sources, 6* (1981) 1.

26a K. J. Euler and B. Seim, *J. Appl. Electrochem.*, *8* (1978) 49.

   b K. Micka and V. Koudelka, *J. Power Sources, 6* (1981) 319.