

History of the use of nonaqueous media in electrochemistry

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Abstract The use of nonaqueous media in electrochemistry is historically reviewed, though the description is based on my personal opinion and is not comprehensive. Here, “media” includes not only organic and inorganic solvents but also ionic liquids and supercritical fluids. The uses in polarography, voltammetry, potentiometry, and related techniques are discussed, but the use in conductimetry is excluded.

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Abbreviations

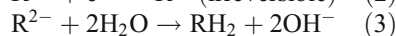
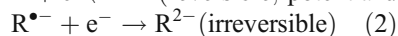
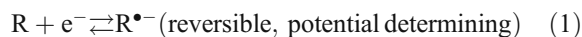
AN	Acetonitrile
γ -BL	γ -Butyrolactone
BMIm	1-Butyl-3-methylimidazolium
BP	<i>N</i> -Butylpyridinium
DME	Dropping mercury electrode
DMF	<i>N,N</i> -Dimethylformamide
DMSO	Dimethyl sulfoxide
EDLC	Electrochemical double-layer capacitor
EMIm	1-Ethyl-3-methylimidazolium
ESR	Electron spin resonance
ET	Electron transfer
EtOH	Ethanol
EV	Electric vehicle
HEV	Hybrid electric vehicle
HMDE	Hanging mercury drop electrode
HMPA	Hexamethylphosphoric triamide
IL	Ionic liquid
ISFET	Ion-selective field effect transistor
ITIES	Interfaces between two immiscible electrolyte solutions
LJP	Liquid junction potential
LUMO	Lowest unoccupied molecular orbital
MeOH	Methanol
MMIm	1,3-Dimethylimidazolium
NB	Nitrobenzene
PC	Propylene carbonate
scCO ₂	Supercritical carbon dioxide
SCF	Supercritical fluid
scW	Supercritical water
UME	Ultramicroelectrode
W	Water

Before 1950

The use of nonaqueous media in polarography began in 1930s. At the beginning, amphiprotic or protic solvents and their mixtures with water were often employed. MeOH and EtOH were the most commonly used nonaqueous solvents. For example, polarographic study in MeOH and EtOH was briefly carried out for dissolved oxygen in 1935 [1] and that in MeOH was carried out for a few cations in 1949 [2]. Polarographic behavior was studied in EtOH–water mixtures about alkali metal ions in 1938 [3], about alkali and alkaline earth metal ions in 1942 [4], and about *p*-nitroaniline in 1949 [5]. A MeOH–benzene mixture was used in 1949 for the polarography of organic peroxides in rancid acid [6]. A 1:1 isopropanol–water mixture with 0.2 M Me₄NOH was used by Wawzonek and Laitinen in 1941 for the polarography of mixtures of benzalacetone and acetophenon [7]. Anhydrous ethylene glycol was used in 1946 for the polarography of dissolved oxygen and several metal ions [8]. Methyl cellosolve (ethylene glycol monomethyl ether) was used in 1950 for polarography and was found to be suitable for the analyses of many nonpolar (low permittivity) organic compounds as well as metal ions [9]. After a preliminary study by MacGillavry in 1936 [10], a systematic study on the use of glacial acetic acid was carried out in 1942 by Bachman and Astle [11]. By using 0.25 M ammonium acetate as supporting electrolyte, they found that metal ions whose half-wave potentials were more negative than -0.3 V vs aqueous (aq.) SCE (Cd²⁺, Zn²⁺, Co²⁺, Cr³⁺, Sb³⁺, and Pb²⁺) yielded normal waves. They also found that benzyl and benzoin produced normal reduction waves in the same supporting electrolyte. Three difficulties existed in the use of glacial acetic acid for polarography: (1) The removal of dissolved oxygen was not easy due to its high solubility; (2) The resistance of the solution was so large that correction for *IR*-drop was necessary; (3) The reduction of hydrogen ion occurred so easily that the half-wave potentials of the depolarizer should be more positive than about -1.4 V vs aq. SCE. In the studies in amphiprotic and protic solvents, the mechanisms of electrode reactions did not differ significantly from those in aqueous solutions; thus, these solvents were used to increase the solubility of organic substances or to investigate the solvent effects on the wave heights and the half-wave potentials.

1,4-Dioxane is an aprotic solvent of low permittivity and is usually used as mixtures with water. Laitinen and Wawzonek used a 75-vol.% dioxane–25% water mixture with 0.175 M (M ≡ mol dm⁻³) Bu₄NI as the supporting electrolyte and studied the reductions of unsaturated hydrocarbons at a dropping mercury electrode (DME) [12, 13]. This solvent had characters in between protic and aprotic: The wave height corresponded to a two-electron reduction

as in water, but the wave analysis showed a reversible one-electron reduction, the half-wave potential being pH-independent, as is often the case in aprotic solvents. Their conclusion was that reaction (1), i.e., the formation of radical anion, was followed by reactions (2) and (3) at the same potential.



Pleskov studied the relation between the electrode potentials and solvation energies of ions, and because the solvation energy decreases with the increase of ion's diameter and the decrease of its charge, he suggested the rubidium electrode as a reference electrode and used it in measuring the electrode potentials in different solvents [14, 15]. Pleskov also reported an Ag/Ag⁺ reference electrode in AN, and this is the first use of dipolar aprotic solvents¹ [15, 16]. But applications of dipolar aprotic solvents in polarography began in 1952, in AN by Wawzonek [17] and in acetone by Arthur and Lyons [18].²

At the end of 1940s, Laitinen and his coworkers [19, 20] used liquid ammonia as a polarographic solvent at -36 °C and with saturated Bu₄NI as the supporting electrolyte. In the studies, Laitinen and Nyman [19] showed that the DME functioned as an “electron electrode” when the cation of the supporting electrolyte was not reducible, the cathodic reaction being the dissolution of electrons from the mercury electrode.

Molten salts were also used as media for polarography and voltammetry. Nachtrieb and Steinberg [21] used a ternary eutectic composed of 66.65 mol% NH₄NO₃–25.76% LiNO₃–7.59% NH₄Cl (melting point, 86.2 °C) at 125.0 °C for the polarographic studies of Ni²⁺, Cu²⁺, and Bi³⁺. Lyalikov and Karmazin [22] used molten KNO₃ (mp 333 °C) and ran voltammetric experiments with a platinum point electrode surrounded by an open-end glass tube. An inert gas bubbled through the mantle tube caused periodic, intermittent immersion of the electrode. The salts of Cd²⁺, Cu²⁺, and Ni²⁺ produced normal current-potential curves whose limiting currents were proportional to the metal concentrations of up to a few tenths of a millimole per mole of KNO₃.

¹ Among the aprotic solvents, those having relatively high permittivities ($\epsilon_r \geq 15$ or 20) or large dipole moments ($\mu \geq 2.5$ D) are usually called “dipolar aprotic solvents.”

² The years when dipolar aprotic solvents became commercially available seem as follows: AN 1952, DMF early 1950s, DMSO 1953, PC 1960, sulfolane 1964, and HMPA 1965.

1951–1960

During this decade, the electrochemistry in nonaqueous media made remarkable progresses. The epoch making was the use of dipolar aprotic solvents in the polarographic reductions of organic compounds. Wawzonek and his coworkers [23, 24] reported in 1955–1956 the use of DMF and AN for the polarographic reductions of anthracene, stilbene, and other compounds. They found that several of the compounds exhibited two one-electron waves in DMF and AN, instead of a two-electron wave that was observed previously in aqueous dioxane [12, 13]. The positioning of the waves was interesting: The two-electron wave in the aqueous dioxane was at approximately the same potential as the first wave in DMF or AN. Moreover, the gradual transition from one-electron reduction to two-electron could be observed by the stepwise addition of water or other weak acids as proton donors. In 1954, Hoijtink and his coworkers [25, 26] observed similar phenomena as in DMF and AN by using 96 vol.% dioxane–4% water mixture, the aprotic property of which was much stronger than that of the 75% dioxane–25% water mixture. The organic compounds in dipolar aprotic solvents were often reduced in two steps, corresponding to one-electron each. The first one-electron step was postulated to be the formation of an anion radical, and the process was considered to correspond to the acceptance of an electron to the lowest unoccupied molecular orbital (LUMO) of the compounds [23–26]. Hoijtink [27] reported a linear relation between the half-wave potentials for the first reduction wave and the energies of LUMO obtained by the calculation method; thus, he opened a method to investigate the LUMO of organic substances by polarographic measurements. Moreover, in 1958, Austen, Given, Ingram, and Peover [28] got the ESR spectrum of anion radicals of anthracene, benzoquinone, and anthraquinone which were electrogenerated in DMF and showed that the postulate was true.³ A series of these reports in dipolar aprotic solvents stimulated many organic chemists to pay attention to the usefulness of polarography (or, more recently, cyclic voltammetry) and of electrochemical-ESR techniques and to run those kinds of experiments by themselves in dipolar aprotic solvents.

The stabilization of anion radicals in dipolar aprotic solvents (AN, γ -BL, DMF, DMSO, HMPA, PC, sulfolane, etc.) occurred due to the fact that the acidity of those solvents were much weaker than that of water. However,

³ By that time, the radical anion for ESR measurement was usually prepared by the reduction of its parent compound (R) with sodium metal, but the ESR signal obtained was often distorted by ion pair ($\text{Na}^+\text{-R}^-$) formation [144]. The electrolytic method by use of tetraalkylammonium salts as supporting electrolyte was free from such ion pair formation.

concerning the basicity of dipolar aprotic solvents, some (AN, PC, sulfolane) are weaker than water, but some (DMF, DMSO, HMPA) are stronger than water. The acid–base properties of solvents give much influence on chemical processes, and the general tendencies are summarized in Table 1 (Chapters 1–4 in [29] for details). By the proper choice of dipolar aprotic solvents, potential window and pH window become much wider than in water, many chemical species that are unstable in water become stable, and many chemical reactions that are slow (fast) in water become fast (slow). Moreover, these favorable influences seemed remarkable in electrochemistry. Many chemists anticipated fruitful results in electrochemistry in dipolar aprotic solvents, and it caused the boom of this field in the next decade.

In 1957, Lund reported voltammetric oxidations of carbinols and aromatic hydrocarbons in AN by using a vibrating platinum electrode as indicator electrode [30]. They did not get a one-electron oxidation wave to radical cation but got a two-electron (actually multi-electron) oxidation wave, because the cation radical was very reactive. In order to observe the formation of radical cations by voltammetry, we had to wait for more 10 years (see the 1961–1970 section).

In this decade, various other progresses were also made. Polarography of inorganic substances was studied in AN briefly by Wawzonek and Runner [17] and in more detail by Kolthoff and Coetzee [31, 32]. Acetone was used in polarography of acid halides (acetyl chloride, etc.) [18]. DMSO was first used in 1959 by Gutmann and Schöber for polarography of various metal ions [33]. Strehlow [34] proposed in 1952, as suggested by Pleskov [14, 15], the potential of the Rb^+/Rb electrode as a solvent-independent standard, but later in 1960, he and his coworkers [35] proposed the potentials of the ferricinium/ferrocene and cobalticinium/cobaltocene couples as solvent-independent standards. The use of ferricinium/ferrocene couple as a solvent-independent potential standard began at this time. In 1958, the solubilities and conductivities of inorganic salts in cyclic esters (ethylene carbonate, PC, and γ -BL) were studied, and these solvents were found to be suitable for electrochemical use [36]. These cyclic esters have been used for lithium batteries since the first half of 1960s. The acid–base equilibria in glacial acetic acid were thoroughly investigated theoretically by Kolthoff and Bruckenstein [37–39], by use of potentiometry as well as spectrophotometry.

1961–1970

In this decade, many electrochemists and electroanalytical chemists were engaged in the studies of electrochemistry in

Table 1 Acid–base properties of solvents and the characteristics of reactions

Solvents with weak (strong) acidity	Solvents with weak (strong) basicity
1) Solvation to small anions is difficult (easy) <ul style="list-style-type: none"> • Small anions are reactive (not reactive) 2) Proton donation from solvent is difficult (easy) <ul style="list-style-type: none"> • pH-window is wide (narrow) on the basic side • Strong bases are differentiated (leveled) • Very weak acids can (cannot) be titrated 3) Reduction of solvent is difficult (easy) <ul style="list-style-type: none"> • Potential region is wide (narrow) on negative side • Strong reducing agent is stable (unstable) in the solvent • Substances difficult to reduce can (cannot) be reduced 	1) Solvation to small cations is difficult (easy) <ul style="list-style-type: none"> • Small cations are reactive (not reactive) 2) Proton acceptance by solvent is difficult (easy) <ul style="list-style-type: none"> • pH-window is wide (narrow) on the acidic side • Strong acids are differentiated (leveled) • Very weak bases can (cannot) be titrated 3) Oxidation of solvent is difficult (easy) <ul style="list-style-type: none"> • Potential region is wide (narrow) on positive side • Strong oxidizing agent is stable (unstable) in the solvent • Substances difficult to oxidize can (cannot) be oxidized

dipolar aprotic solvents from various standpoints. Organic and inorganic chemists began to use polarography or cyclic voltammetry (at a platinum electrode or a hanging mercury drop electrode (HMDE)) in dipolar aprotic solvents routinely as a method to know the electronic states of organic and organometallic substances. Naturally, the number of reports suddenly increased: Only a few topics among them will be described here.

Dissolved oxygen in dipolar aprotic solvents was found to form an anion radical (superoxide ion) by one-electron reduction. Due to the chemical and biological importance of the superoxide ion, several reports appeared at a time using polarography and cyclic voltammetry at a platinum electrode [40–44]. The superoxide ion gave an ESR signal, as many anion radicals of organic substances do. It formed an ion pair with alkali metal ions, and the half-wave potential for the oxygen reduction was shifted to positive direction. The transition from one-electron process to two-electron process could be observed by the addition of proton donors.

By cyclic voltammetry at a platinum electrode in AN, 9,10-diphenylanthracene was found to give two-step oxidation processes of one-electron each, and the first step of which was shown to correspond to the formation of a cation radical [45]. The cation radical of 9,10-diphenylanthracene is much more stable than that of anthracene because the 9- and 10-positions, which are reactive because of the high unpaired electron densities, are masked by phenyl group, and unpaired electrons are delocalized. An ESR signal was observed for the cation radical. In order to realize a one-electron reversible oxidation of anthracene, cyclic voltammetry at a Pt ultramicroelectrode (UME) in AN-Et₄NClO₄ should be measured at a very rapid scan rate (10,000 V s⁻¹), a multielectron oxidation step being observed at 100 V s⁻¹ [46].

During this decade, the instruments for polarography and voltammetry gradually shifted from the two-electrode type to the three-electrode type by the use of operational

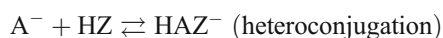
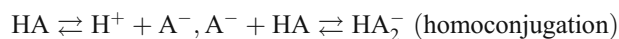
amplifiers. This was very suitable for the measurements in nonaqueous solutions, because, with the three-electrode type, the cell resistance, which was usually high in these solutions, did not give significant influence to the current-potential curves. The three-electrode instrument was also convenient in that the reference electrodes could be much smaller in size and higher in solution resistance. Irrespective of two- or three-electrode instrument, two types of reference electrodes have been used—one is the reference electrode that uses the same solvent as that of the test solution, and the other is the use of aqueous reference electrodes (aqueous SCE and Ag/AgCl electrodes),⁴ though the use of aqueous reference electrodes should be avoided, if possible, because the liquid junction potential (LJP) between aqueous and nonaqueous solutions makes the potential measurement uncertain (see the 1971–1980 section). It should be mentioned that, during this decade, a large number of reference electrodes that used the organic solvents under study were reported [47], though many of them were not used repeatedly.

In 1966, HMPA, an aprotic solvent of strongest basicity, was used by Dubois et al. [48] for voltammetry at a rotated platinum electrode. They reported about the potential windows in various supporting electrolytes and the reference electrodes (Ag/Ag⁺ and Ag/AgCl) which used HMPA (for interesting topics in HMPA, see the 1971–1980 section). As other dipolar aprotic solvents, sulfolane (tetramethylene sulfone) was used in 1967 for polarography [49] and *N*-methyl-2-pyrrolidinone in 1968 for voltammetry [50].

Beginning from 1963 and continuing till the middle of 1970s, Kolthoff, Chantooni, and their coworkers [51–53] reported a series of detailed studies on acid–base equilibria

⁴ Recently, Ag/Ag⁺ electrode in AN is sometimes used as a reference electrode by inserting it into other dipolar aprotic solvents. In this case, the influence of the LJP is much smaller than the case of aqueous reference electrode.

in AN, DMF, DMSO, and PC. The methods employed included potentiometry at a pH glass electrode. Many phenomena, which are different from the acid–base equilibria in water (or protic solvents), became apparent. Among them are the formations of homo- and heteroconjugated species.



Due to the presence of conjugated species, the common knowledge of acid–base equilibria in water is completely inapplicable in dipolar aprotic solvents. These studies were important because they helped to understand the chemistry in dipolar aprotic solvents correctly.

High energy batteries (mainly lithium batteries) were investigated from the beginning of 1960s, but most of the results were published as governmental reports, principally of the Department of Defense and NASA of USA, or as patent literatures. The situations of these investigations have been described in the book of Jasinski [54]. The organic solvents, which attracted the most attention, were cyclic esters, like PC and γ -BL, and linear esters, like methyl formate, methyl acetate, and ethyl acetate. The high energy batteries needed, in addition to highly efficient electrolyte solutions, highly efficient negative (Li) and positive electrodes. At that time, however, truly satisfactory combinations of them were still not available.

1971–1980

In this decade, the enthusiasm for the electrochemistry in nonaqueous solvents gradually subsided, but the use of nonaqueous solvents still continued at high levels. Especially, the cyclic voltammetry in dipolar aprotic solvents become a popular technique among the organic and organometallic chemists. For recent reviews on the historical aspects of electrochemistry of organic and organometallic substances, see [55] and [56].

The studies on lithium batteries became very popular since the beginning of 1970s [57], and two companies of Japan (Matsushita and Sanyo) began to sell primary lithium batteries to the general public in 1976 [58, 59]. The batteries of Matsushita composed of the anode of Li metal, the cathode of carbon monofluoride (CF)_n, and the electrolyte of LiBF₄ in γ -BL or in PC + tetrahydrofuran. In the case of Sanyo, the anode was Li metal, the cathode was MnO₂, and the electrolyte was LiClO₄ in PC + dimethoxyethane (1:1 by volume). The batteries were cylindrical type or flat type and were mainly used for calculators, watches, and cameras. The efforts for develop-

ing secondary (rechargeable) lithium batteries were beginning, but, for the appearance of satisfactory ones, we had to wait till the beginning of 1990s.

HMPA is the strongly basic solvent as described in the 1961–1970 section, and in 1971–1972, two interesting results in it were reported. One is about solvated electrons. HMPA is known to be the only solvent that solvated electrons can exist at room temperatures: When sodium metal is thrown into HMPA, it dissolves forming bluish solvated electrons.⁵ The solvated electrons can also be generated from the electrode at very negative potential, and the electrode reactions of the process were studied in detail [60]. Another is about the influence of the cation of the supporting electrolytes. Tetraalkylammonium salts had been considered to be versatile as supporting electrolytes in dipolar aprotic solvents, giving no harm to the electrode reactions. But a problem was observed in HMPA: tetraethyl- and tetramethylammonium ions in HMPA inhibited the reductions of lithium and sodium (and partly potassium) ions at the DME by “electrochemical masking” [61, 62]. These metal ions are strongly solvated in HMPA, and their sizes are larger than those of tetraethyl- and tetramethylammonium ions; thus, at very negative potentials at which the reductions of these metal ions should occur, these tetraalkylammonium ions are more easily attracted electrostatically to the surface of the DME and mask the reduction of these metal ions. This phenomenon was observed very clearly in HMPA, but it became apparent that the phenomenon could occur to a lesser extent even in other basic dipolar aprotic solvents. Thus, the general belief that tetraalkylammonium salts are the versatile supporting electrolytes in dipolar aprotic solvents was denied. Unfortunately, in 1976, it was reported that HMPA might cause cancer and heritable genetic damages [63], and since then, its use was almost banned.

In 1972, the techniques of low-temperature electrochemistry were developed [64]. They are useful in studying electrode reactions involving unstable products or intermediates of organic compounds and metal complexes. Lowering the temperature by 30–40 °C decreases the reaction rate of the unstable species to one tenth of the original value. It is equivalent to a ten-fold increase in the voltage scan rate of cyclic voltammetry. The practical aspects of low-temperature electrochemistry have been reviewed [65]. The lowest temperature hitherto obtained is –185 °C in butyronitrile/ethylchloride (1:1 by volume) with 0.2 M Bu₄NClO₄ as the supporting electrolyte. Some specific situations occur for voltammetry at low temperatures: increase in solution

⁵ Three cases occur when the sodium metal (Na) is thrown into solvents: (1) the case where Na is dissolved generating hydrogen gas, (2) the case when Na remains unchanged, and (3) the case when Na dissolves forming solvated electrons. The last occurs in ammonia (bp –33.4 °C), methylamine (bp –6 °C), and HMPA (bp 233 °C).

resistance, decrease in the rate of diffusion of electroactive species, decrease in the Nernstian slope, etc., and appropriate care must be taken for them. The use of an UME is useful to overcome the influence of solution resistance.

As described in the 1961–1970 section, two types of reference electrodes are used for electrochemistry in nonaqueous solutions. Because the use of aqueous reference electrodes actually occurs quite often, the problem of the LJP between aqueous and nonaqueous solutions is a matter of concern. Estimation of the LJP between aqueous and nonaqueous solutions has been carried out by applying extrathermodynamic assumptions [66, 67]: for example, Diggle and Parker estimated the LJPs between saturated aqueous KCl and 0.1 M Et₄NPic(S) (Pic = picrate, S = organic solvent) by assuming that $\Delta G_t(\text{Ph}_4\text{As}^+) = \Delta G_t(\text{BPh}_4^-)$, where $\Delta G_t(i)$ shows the Gibbs energy of transfer of ion *i* between water and organic solvent [67].⁶ But these could not clarify the details of the LJP between different solvents. Several reports appeared during this decade intending to elucidate the components of the LJP between different solvents, but they were not satisfactory enough [68–72].⁷ Here, I briefly outline the results of our study which was done intermittently from 1970s till 2010 (see [73–76] and Section 6.4 of [29]).

The LJP between different solvents consists of three components, i.e., component (a) due to electrolyte concentrations and ionic mobilities, component (b) due to the solvation of ions, and component (c) due to solvent–solvent interactions. Component (a) is somewhat similar to the LJP between solutions in the same solvent, but components (b) and (c) are specific to the junction between different solvents.

We first consider a free-diffusion junction with the same electrolyte on the two sides ($c_1 \text{MX}(S_1)/c_2 \text{MX}(S_2)$). The characteristics of the three components are schematically shown in Fig. 1. Under appropriate experimental conditions, we can measure the variation in each of the three components separately. Thus, we can study the characteristics of each component. Components (a) and (b) are diffusion potentials. Component (a) is due to the diffusions of ions by the gradients in ionic concentrations, and its actual values agree with the values calculated from the Henderson equation, which was derived in the same way as the Henderson equation at the junction between the same solvent. Component (b) is due to the ionic diffusions by the

gradients in ionic standard chemical potentials or ionic solvation energies and is independent of electrolyte concentrations. However, its actual values are much smaller than the values calculated from theoretical equation derived in the same way as the equation for component (a); i.e., the actual values were about a half of the theoretical values for miscible water/aprotic solvent junctions,⁸ almost equal to zero for the junctions between two aprotic solvents, and in between the two extremes for other junctions. This disagreement between the actual and theoretical values is considered to be related to that the ionic diffusion occurs as the result of ionic random-walk in the solvent, the average time and distance of a step being extremely small [75]. Component (c), which is due to the solvent–solvent interactions at the junction, is nearly electrolyte-independent. It is a dipole potential, and its characteristics can be understood if we consider that the two solvents at the junction interact with each other as a Lewis acid and a Lewis base, and some of the solvent molecules are oriented perpendicularly to the interphase (see component (c) in Fig. 1): The solvent side as a Lewis acid is more negative than that as a Lewis base, and the value increases with the increase of the strength of the solvent interaction. Here, the value of each of the three components can be estimated separately from the others, and the total LJP can be obtained by summing them up.⁹ Experimentally, the LJP reaches a steady value within a few seconds, it is reproducible within ± 1 mV, and although the thickness of the junction expands with time by the mutual diffusion of solvents and electrolytes, it is very stable (the drift is within ± 1 mV/h even when the LJP is near to 200 mV) as far as the electrolytes on the two sides are the same.

Even when the electrolytes on the two sides are of different kinds, if the concentration on one side is more than 20 times that on the other and if the junction is a free-diffusion type, the LJP is determined by the more concentrated electrolyte, and it is stable with time. This justifies, to some extent, the use of aqueous reference electrodes for the measurements in nonaqueous solutions.

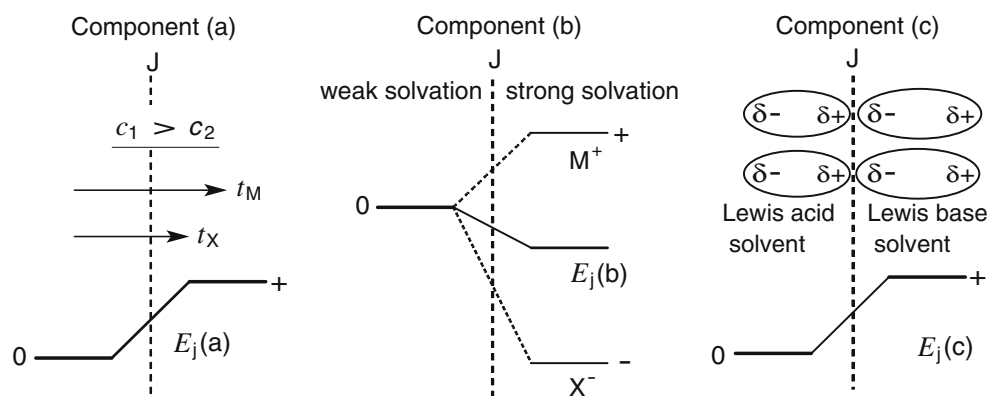
⁶ The LJP estimated was 172 mV for DMSO, 174 mV for DMF, 93 mV for AN, and 25 mV for MeOH, with the water side more negative.

⁷ All research groups in [68–72] assumed the existence of the three components, similar to us, but they considered that all of the three were diffusion potentials, which are related to the ionic transfer across the junction between different solvents. According to our studies, this is not correct as described below, i.e., component (c) is a dipole potential.

⁸ The actual value and the theoretical value agree to each other at immiscible junctions, at which the interphase region varies not gradually but abruptly.

⁹ The magnitude of component (a) varies with the variation in c_1/c_2 , and for its variation from 100 mM/1 mM to 1 mM/100 mM, it varied between ca. +40 mV and ca. –40 mV. The actual value of component (b) varies with the species MX: the largest variations were ca. 354 mV at H₂O|PC, 254 mV at H₂O|AN, and 192 mV at H₂O|DMF between MX of NaPh₄B and Bu₄NCl and 172 mV at H₂O/DMSO between MX of Me₄NClO₄ and LiCl. Component (b) may be the biggest among the three components. Component (c) varies with S₁/S₂: the value was 122 mV for H₂O/DMF and H₂O/DMSO, 44 mV for H₂O/AN and 30 mV for H₂O/PC (at $c_1 = c_2 = 1$ mM), as estimated under the assumptions that the values of component (c) at H₂O/NB and AN/aprotic solvents equal zero.

Fig. 1 Three components of the LJP between electrolyte solutions in different solvents.
Junction: $c_1 \text{MX}(\text{S}_1) | c_2 \text{MX}(\text{S}_2)$



In reality, however, the junctions between different solvents are, in many cases, not free-diffusion type but are restrained with a sintered-glass or ceramic plug. The situation is thus complicated: the composition of solvents and electrolytes in the plug is indefinite, and sometimes, a clog of electrolyte is formed, making the LJP less reproducible and less stable. This applies to the case when an aqueous reference electrode is inserted in a nonaqueous solution.

1981–1990

The salt *N*-butylpyridinium chloride– AlCl_3 was found to be a good ionic liquid in 1978 [77], and the electrochemical use of chloroaluminate ionic liquids (ILs) began in 1979 [78–80]. Here, ILs or room temperature ionic liquids (RTILs) are the salts that are liquids near room temperatures or below 100 °C. Chloroaluminate ILs are mixtures of AlCl_3 and organic chloride (R^+Cl^-), where R^+ are 1,3-dimethylimidazolium ($[\text{MMIm}]^+$), 1-ethyl-3-methylimidazolium ($[\text{EMIm}]^+$), 1-butyl-3-methylimidazolium ($[\text{BMIm}]^+$), 1-propyl-2,3-dimethylimidazolium ($[\text{PMMIm}]^+$), *N*-butylpyridinium ($[\text{BP}]^+$), etc. The reaction $2\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^- + \text{AlCl}_3 \rightarrow \text{Al}_2\text{Cl}_7^-$ occurs between AlCl_3 and Cl^- . If the mole fraction of AlCl_3 is expressed by N ($\equiv [\text{AlCl}_3]/([\text{AlCl}_3] + [\text{RCl}])$), the ILs of $N=0.5$ are neutral with an anion AlCl_4^- , the ILs of $N>0.5$ are acidic with anions Al_2Cl_7^- and AlCl_4^- , and the ILs of $N<0.5$ are basic with anions AlCl_4^- and Cl^- . The studies on electrochemistry in chloroaluminate ILs were active in 1980s and 1990s, and the ILs were used, in addition to the fundamental studies, to practical applications such as electrolytic depositions of metals, alloys and semiconductors, electrolytic syntheses of organic substances including conductive polymers, and in electrochemical devices (rechargeable lithium batteries, supercapacitors, photocells, etc.). Chloroaluminate ILs are nonflammable but have a demerit that they are hygroscopic and must be used by avoiding moisture. For reviews of electrochemistry in chloroaluminate ILs, see [81–83].

Electrochemistry at the interfaces between two immiscible electrolyte solutions (ITIES) began in 1974 by the report of Gavach and his coworkers [84–86]. They studied chronopotentiometrically the transport of tetraalkylammonium ions at the interface (W/O) between water and nitrobenzene. In 1976–1977, Koryta and his group (Samek, Mareček) studied the electrochemistry at ITIES by polarography at the dropping electrolyte electrode and by cyclic voltammetry [87–89]. From the beginning of 1980s, many researchers (Girault, Kakiuchi, Kihara, Schiffrin, Senda, etc.) joined in the studies of this subject. Great progresses were made in both theoretical and experimental aspects, and the ITIES became one of the major research targets in electrochemistry. In addition to ion transfers, electron transfers and couples of ion/electron transfers could be investigated. Besides nitrobenzene, 1,2-dichloroethane, *o*-nitrophenol octylether, and other organic solvents, that are immiscible with water, were used as O of the W/O interface. The ion transfer processes were applicable to the analyses of various ionic species, especially the redox-inactive biological and pharmaceutical species being promising targets. They were also useful to get fundamental data of the ion transfer processes, which could be applied in the separation chemistry, in the elucidation of biological membrane processes and in the fabrication of ion-selective electrodes. Charge transfer processes, including an intermediate or a product adsorbed at the interfacial region, were of practical interest: they could be used to electropolymerizations, electrodepositions of noble metals, and others. For more recent topics in this field, see the 2001–2010 section.

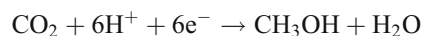
An ultramicroelectrode (UME) has been used since 1950s for a Clark electrode in order to determine dissolved oxygen contained in biological tissues [90]. However, the UMEs became very popular in 1980s as indicator electrodes for voltammetry, being supported by sound theoretical backgrounds [92, 93]. They are especially convenient for use in nonaqueous solutions. Firstly, because the current that flows at a UME is extremely small (10 pA–100 nA),

we can keep the effect of the *IR*-drop very small and can measure voltammograms even in solutions of high resistances. Cyclic voltammetry is possible in solutions of nonpolar solvents such as benzene, toluene, hexane, and heptane and in the gaseous phase and supercritical fluids (SCFs). The voltammetry in the solution without supporting electrolyte is also possible: in AN without supporting electrolyte, the positive end of the potential window reached +6 V vs Ag/Ag⁺ electrode in AN and electrolytic oxidations of substances with high ionization potentials, such as methane, butane, pentane, heptane, rare gases (Ar, Kr, Xe), and oxygen, were possible. In SO₂ at -70 °C and without supporting electrolyte, Cs⁺, Rb⁺, K⁺, and Na⁺ could be oxidized at a platinum UME (10 μm in diameter). Secondly, because the current that flows at the UME is so small, we can scan the electrode potential at extremely high rates, sometimes reaching 1,000,000 V s⁻¹ or even more. By using cyclic voltammetry at such fast scan rates, we can detect intermediates and products with very short lifetimes and study their thermodynamic and kinetic properties. For the case of oxidation of anthracene, see the 1961–1970 section. We can also determine the rate constants of very rapid electrode reactions. As an extreme case, an UME of 1–2 nm in size is called nanode or nanoelectrode [94] and is suitable for determining the rate constants of very fast electrode reactions. For example, the standard rate constant has been obtained to be 220±120 cm s⁻¹ for the ferrocenium/ferrocene couple in AN–0.3 M Bu₄NClO₄, though this value is extremely large among the literature values for the same couple [95].

Contrarily, during this period, the use of mercury electrodes (DME, HMDE, etc.) was gradually restricted or banned in many laboratories, due to the environmental hazard of mercury. Polarography that uses a DME thus lost its popularity.

In 1981, Silvestri et al. [96] used supercritical HCl and NH₃ for studying the anodic dissolutions of Fe and Ag. Since then, electrochemical studies in SCFs have been carried out to a considerable extent. Bard and his coworkers [97–100] carried out voltammetric works in supercritical water (scW) as well as in near-critical water. High temperature water is very corrosive, attacks most metals, and dissolves quartz and Pyrex glass, leading to equipment failure and solution contamination. Thus, they used an improved cell which was resistive to scW. Because scW and near-critical water have low permittivity and can dissolve many nonpolar organic compounds, electrochemical organic syntheses in these media is promising. Bard and his coworkers [101–103] also studied electrochemistry in near-critical and supercritical NH₃, SO₂, and AN. Super critical carbon dioxide (scCO₂) is important in that it is nontoxic, nonflammable, environmentally benign, commercially available in high quality, and has easily attainable critical

parameters. However, it is practically nonpolar (ε_r~1.6), and polar solutes and electrolytes are difficult to dissolve in it. Voltammetric measurements in scCO₂ are usually carried out by adding some polar modifier (e.g., H₂O, AN) to increase the polarity. Wightman and his coworkers [104] studied, using UMEs, the voltammetric oxidation of ferrocene in scCO₂ containing H₂O as a modifier and Hex₄NPF₆ as a supporting electrolyte. In 1997, Li and Prentice [105] used a high-pressure, near-critical CO₂ + H₂O + EtOH solution, with LiCl as electrolyte and copper as cathode, to synthesize MeOH by direct electrochemical reduction of CO₂.



Supercritical difluoromethane (HFC32), trifluoromethane (HFC23), and 1,1,1,2-tetrafluoroethane (HFC134a) are somewhat more polar than scCO₂ and have readily attainable critical parameters. In 1990s, these SCFs were used as voltammetric solvents alone or by mixing with CO₂. Olsen and Tallman [106, 107] measured in supercritical chlorodifluoromethane and HFC23 the oxidation wave of ferrocene (Fc⁰→Fc⁺) and the reduction wave of cobaltocenium ion (Cc⁺→Cc⁰). The difference between their half-wave potentials was 1.28 V, in fair agreement with 1.31 V obtained as an average in various nonaqueous solvents [108]. Abbott and his coworkers carried out a series of studies. By using HFC134a and HFC32 in liquid and supercritical states, oxidation waves of Cs⁺ and Xe were obtained [109]. The width of the potential window in HFC134a + 0.1 M Bu₄NClO₄ was 9.4 V in liquid at 30 °C and 10 bar.

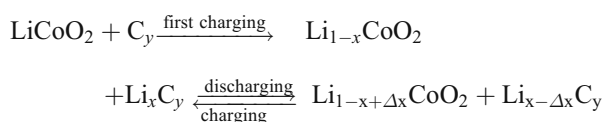
Up to now, the use of SCFs in electrochemical technologies is still scarce but is expected to become more popular as an electrochemical media which is benign to the environment.

During this decade, IUPAC Commissions on Electrochemistry and Electroanalytical Chemistry published various reports on electrochemistry in nonaqueous solutions. Gritzner and Kuta [110] published a method for reporting the potentials in nonaqueous solutions, in which ferricinium ion/ferrocene and bis(biphenyl)chromium(I)/(0) couples were recommended as potential standards. Mussini et al. [111] reported the method recommended for measuring the pH of the solutions in organic solvents of high permittivity and in water-organic solvent mixtures. A booklet on the methods for purifications of various solvents for electrochemical use was edited by Coetzee [112], and at the same time, many other reports on solvent purifications were published in the journal of IUPAC, Pure and Applied Chemistry. Izutsu [113] compiled a databook on acid–base dissociation equilibria in dipolar aprotic solvents.

1991–2000

The reaction of the Li^+/Li electrode in lithium batteries can be reversible. Thus, the lithium primary batteries are rechargeable, if a reversible cathode is applicable. However, the Li^+/Li electrode has a problem that the lithium metal loses its smooth surface by repeated charging/discharging cycles, forming dendritic deposits, which may cause an internal electrical short-circuit between the anode and the cathode.

In the lithium-ion battery (rechargeable lithium battery), which was put on the market by Sony in 1991, the difficulty of the Li^+/Li electrode was avoided by use of a carbon anode (C_y), which worked as a host for the intercalation of Li^+ ions [114]. The active materials for the cathode were LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and LiFePO_4 , which also worked as a host for Li^+ ions. Electrolyte solutions in the primary lithium batteries could also be used, in principle, in lithium-ion batteries. But the majority of manufacturers used electrolyte solutions composed of LiPF_6 , ethylene carbonate, and one or more linear carbonates from dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate, although one manufacturer used ($\gamma\text{-BL} + \text{LiBF}_4$) as an electrolyte solution. The addition of linear carbonate(s) was effective to increase the fluidity and reduce the melting point of the electrolyte solution. The reaction at the cathode of LiCoO_2 is as follows:



In the charging process, Co(III) in LiCoO_2 was oxidized to Co(IV). This battery had a working voltage of ~ 3.7 V and a cycle number of >1000 .

Lithium-ion batteries of small to moderate sizes have widely been used as power sources for computers, telephones, cameras, camcorders, etc. For the applications of large-size lithium-ion batteries, see the 2001–2010 section.

The dynamic effect of solvents on electron transfer (ET) processes ($\text{Ox} + \text{e}^- \rightarrow \text{Red}$) is also an interesting topic [115–117]. According to the Marcus' model, the standard rate constant, k_s , for the ET process can be expressed as follows, if it is an adiabatic outer-sphere process:

$$\ln \frac{k_s}{(\Delta G^*)^{1/2}} + \frac{\Delta G^*}{RT} = \ln \frac{\kappa K_p}{(4\pi RT)^{1/2}} + \ln \tau_L^{-1}$$

where κ is the transmission coefficient (~ 1), K_p is the pre-equilibrium constant that describes the statistical probability of the formation of an electrode-reactant configuration that is appropriate to the electrode reaction, τ_L is the longitudinal solvent relaxation time, ΔG^* is the activation energy,

and $\Delta G^* = \Delta G_{\text{is}}^* + \Delta G_{\text{os}}^*$. ΔG_{is}^* is the inner-shell activation energy due to the reorganization of reactant itself while ΔG_{os}^* is the outer-shell activation energy due to the reorganization of the solvent around the reactant, and here, we assume that $\Delta G_{\text{os}}^* \gg \Delta G_{\text{is}}^*$. Then, the following relations should exist:

- (1) The relation between $\{\ln[k_s/(\Delta G_{\text{os}}^*)^{1/2}] + \Delta G_{\text{os}}^*/RT\}$ and $\ln \tau_L^{-1}$ for various solvents is expected to be linear, with a slope of unity for an adiabatic process.
- (2) If the dynamic component predominates, a near-linear relation can be expected between $\ln k_s$ and $\ln \tau_L^{-1}$.

Both of these relations have been confirmed experimentally using electrode processes of large organic compounds (e.g., the reductions of *p*-dicyanobenzene and benzophenone) and organometallic compounds (e.g., the oxidation of nickelocene and the reductions of Cc^+ to cobaltocene (Cc) and of Cc to Cc^-). It is fascinating that the solvent relaxation time, of pico- to femtoseconds, which is related to solvent reorganization around the reactant, plays an important role in determining the rates of the ET processes. Similar relations have also been observed for the homogeneous self-exchange ET process ($\text{Ox}_1 + \text{Red}_1^* \rightarrow \text{Red}_1 + \text{Ox}_1^*$).

An interesting electrode reaction is the reduction of Buckminsterfullerene (C_{60}) [118, 119]. In AN/toluene at -10 °C, it gives six one-electron reversible steps in cyclic voltammetry at 100 mV s^{-1} . C_{60} can accept up to six electrons to form diamagnetic C_{60}^{6-} , because its LUMO is triply degenerated.

Combinations of electrochemical and nonelectrochemical techniques also made big progresses in this decade. Among them are applications of spectroelectrochemistry, electrochemical ESR, electrochemical mass spectroscopy, electrochemical quartz crystal microbalance, and scanning electrochemical microscopy. They contributed to the elucidations of electrode processes in nonaqueous solutions (see Chapter 9 of [29]): especially, the use of stopped-flow methods was effective in studying the behavior of short-lived radical cations [120, 121].

In potentiometric studies of acid–base equilibria in nonaqueous solvents, a pH glass electrode is generally used as an indicator electrode, but its response in basic dipolar aprotic solvents (e.g., DMSO) is usually very slow, in some cases taking over an hour to reach a steady potential. This problem was solved by the use of a pH-ISFET, which could respond very rapidly (almost instantaneously) even in such solvents [122, 123].

2001–2010

Most ionic liquids (ILs) are divided into chloroaluminate ILs and nonchloroaluminate ILs. We discussed in the

1981–1990 section about chloroaluminate ILs. Nonchloroaluminate ILs are the salts between an organic cation R^+ and an anion A^- , where R^+ is $[MMIm]^+$, $[EMIm]^+$, $[BMIm]^+$, $[BP]^+$, 1-butyl-3-methylpyridinium ($[BMP]^+$), 1,1-dimethylpyrrolidinium ($[MMPyr]^+$), trimethylethylammonium ($[Me_3EtN]^+$), etc., and A^- is BF_4^- , PF_6^- , $CF_3SO_3^-$, $(CF_3SO_2)_2 N^-$, etc. In 1992, $[EMIm]^+$ -based ILs ($[EMIm]BF_4$ and $[EMIm]MeCO_2$) were reported to be air- and water-stable low melting salts [124]. Since then, nonchloroaluminate ILs have been used as solvents in many fields, including electrochemistry. The electrochemical results in nonchloroaluminate ILs have been published in 2000s much more than in 1990s, and the number of publications is still increasing. Several books appeared recently regarding the fundamentals of electrochemistry in ILs and their practical applications [81–83]. Because many cations R^+ and many anions A^- can be combined to form ILs, the number of nonchloroaluminate ILs is really endless. Many of them are nonvolatile, nonflammable, chemically and thermally stable, and good solvents for both organic and inorganic materials. From electrochemical standpoints, they have good electrical conductivities and wide potential windows. The widest potential windows obtained with the ILs composed of aliphatic quaternary ammonium cations and fluoroanions are nearly 6.0 V, which compares to the potential windows in dipolar aprotic solvents. Usually the hydrogen bond acidities of nonchloroaluminate ILs range from aprotic to a little higher than aprotic, while their basicities are near to or even lower than that of acetonitrile, which is very weakly basic.¹⁰ Hydrophobic ILs can be washed with water, and they can be used repeatedly, though the water content in them may change. They form interfaces with water (W) and are applicable to chemical separations, extractions, and electrochemistry at the W/IL interfaces (see below). Voltammetric investigations of various inorganic and organic depolarizers have been carried out in ILs. In most cases, the voltammetric behaviors resemble those in dipolar aprotic solvent of weak acidity, though the diffusion coefficients are smaller than those in dipolar organic solvents because of the high viscosities. The nonchloroaluminate ILs have been applied to various electrochemical technologies: they have been used in electrodepositions of metals, alloys and semiconductors, electrochemical syntheses of conducting polymers and organic compounds, and in preparing various electrochemical devices such as rechargeable lithium batteries, electrochemical double-layer capacitors, electrochromic

devices, and electrochemical mechanical actuators, but the interest to these applications is still mainly academic [81]. Nonchloroaluminate ILs are said to be more green substitutes for conventional volatile organic solvents. This is mainly because the ILs are believed to be nonflammable and less toxic due to their nonvolatile properties. Certainly, air pollution will be reduced by use of these ILs, but recently their risks to the aquatic systems and soils have been pointed out [125]. The toxicities of imidazolium ILs are said to be analogous to ammonia and phenol, which are fairly toxic. These ILs, if leak out, may be more damaging to aquatic ecosystems than conventional volatile organic solvents. The methods to make the wastes of ILs harmless must be established (see Section 13.3.4 of [29]).

Studies on lithium-ion batteries have also made big progresses in 2000s [114, 126]. Especially, the developments of sophisticated large-size lithium batteries, which are to be used for electric vehicle (EV) and hybrid electric vehicle (HEV), have been very active. It is because EV and HEV are very important to save fossil fuels and to protect the global environment by decreasing carbon dioxide emissions and lithium-ion batteries play key roles in them. The industries of lithium-ion batteries are now expanding very rapidly, mainly to manufacture large-size lithium batteries for EV and HEV, and many new factories for it are now being established. Connected with this, the electrolytes for such large-size batteries have been improved, low flammability being the main required properties. Two methods are available in getting low flammable electrolytes: one is to add additives to the electrolyte solutions, and the other is to use new solvent/electrolyte systems. To get low flammability by additives, gas-evolving ingredients or phosphorous-based organic molecules are used. In order to get low flammability by new solvents, fluorinated esters and fluorinated carbonates may be used, alone or as a cosolvent. The use of fluorinated solvents improves, in addition to nonflammability, the low-temperature performances. The use of ILs is also a method to make rechargeable lithium batteries nonflammable: the batteries that use ILs are at present somewhat inferior in performances to those that use nonaqueous solvents, though improved ILs may appear in the future. In addition to such liquid electrolytes, polymer type and plastic-sheet type lithium batteries have also been developed.

The use of nonaqueous solvents in supercapacitors (electrochemical double-layer capacitors (EDLCs) and pseudocapacitors) also made big progresses [127, 128]. In the EDLCs of nonaqueous electrolyte solutions (typically 0.5–1.0 M Et_4NBF_4 in PC) with potential windows larger than 5 V, the value of the charging voltage (ΔV) reaches 3.5–4.0 V. It is a big advantage over aqueous electrolyte solutions (e.g., H_2SO_4), for which ΔV is 1.0–1.5 V. The

¹⁰ There are protic ILs too, the cations R^+ of which being primary, secondary, and tertiary ammonium cations, 1-alkylimidazolium cations, 1-alkyl-2-alkylimidazolium cations, etc.

merits of EDLCs over secondary batteries are the long cycle lives (10^6 or more) and the possibility of rapid charging/discharging. They are because the processes at the EDLCs are mainly capacitive, and the surfaces of the carbon electrodes are not influenced by the repeated charging/discharging processes. Recently, carbon materials with large surface area have been prepared by use of carbon nanotubes and others. The EDLCs that use ILs have also been studied [129]. Pseudocapacitors use metal oxides or redox polymers as electrodes. In pseudocapacitors of redox polymers, nonaqueous electrolyte solutions (typically $\text{Et}_4\text{NBF}_4\text{-PC}$) are often employed, and the charging/discharging processes are mainly faradaic in nature. Recently, highly effective energy storage has been achieved with a cell called an asymmetric hybrid capacitor: a combination of an EDLC electrode and a battery-like electrode, which works pseudocapacitive, form a capacitor [130, 131]. For example, with a combination of an activated carbon electrode (anode) and a graphite carbon electrode (cathode) in 1 M $\text{Et}_4\text{NBF}_4\text{-PC}$, energy density of over 20 Wh kg^{-1} could be obtained, in contrast to less than 4 Wh kg^{-1} for conventional EDLC. Here, the intercalation of anions makes the graphite electrode pseudocapacitive. These large size capacitors, using nonaqueous electrolytes, will play a supplementary role of rechargeable lithium batteries in EVs and HEVs.

The studies on ITIES also continued, and for example, a flow-cell for rapid coulometric ion-transfer at the W/O interface was developed [132] and was used for analytical purposes. Two other topics are interesting. One is the electrochemistry at the interface between water and hydrophobic ionic liquid (W/IL) [133, 134]; here, the organic solvent and the supporting electrolyte of the ITIES have been replaced by an IL. As a byproduct of this study, Kakiuchi and his coworkers proposed an IL salt bridge [135] and an Ag/AgCl reference electrode, based on an IL saturated with AgCl [136], for use in purely aqueous solutions. The other is the three-phase electrochemistry: Scholz [137] developed this method in 2000 as a means to study Gibbs energies of transfer of ions across liquid/liquid interfaces and several groups (Compton, Bond, Girault, Stojek) joined in the same study. A few types of cells have been used: all of them involve three phases in contact, one is the working electrode (flat or cylindrical type; metal or graphite) and the other two are liquids that are immiscible (O and W). Besides the working electrode, two electrodes (reference and auxiliary) are used, though, in conventional electrochemistry at the ITIES, four electrodes (two references and two auxiliaries) are used besides the electrode of the W/O interface. During the electrode process, an ion moves across the boundary between O and W. For the reviews and some of more recent reports, see [138–141].

Many researchers in academic and industrial chemical fields are now searching for new solvents or media that can reduce or eliminate the intrinsic hazards associated with traditional solvents. This is also the case in electrochemistry. According to the principles of Green Chemistry [142], the following strategies can be adopted: (1) using solvent-free systems, (2) replacing organic solvents by water or aqueous solutions, (3) using reduced-hazard organic solvents, (4) using immobilized solvents, (5) using fluorous (= perfluorinated) solvents, (6) using super- and subcritical fluids, and (7) using ionic liquids.

Of course, solvent-free systems are an ultimate solution for avoiding hazards of solvents. But these systems are not realistic in electrochemistry. Moreover, water, the most popular solvent, is protic and not appropriate for processes that need aprotic environments. Reduced-hazard organic solvents are in real use: among them are some solvents that are newly designed and developed, fluorinated organic solvents adopted in rechargeable lithium batteries being such examples. Immobilized solvents have also been used in rechargeable lithium batteries. The electrochemistry in fluorous solvents is just at its beginning [143]. For example, in order to carry out voltammetric measurements in perfluoromethylcyclohexane, a fluorous solvent of permittivity (ϵ_r) ≈ 1 , two strategies have been utilized: one is to add another fluorous solvent, benzotrifluoride of $\epsilon_r=9.2$, in 1:1 ratio in order to get a mixture with a modest ϵ_r value, and the other is to use, as a fluorophilic supporting electrolyte, a salt consisting of an imidazolium cation with a fluorous ponytail and a lipophilic anion, tetrakis(3,5-tri-fluoromethyl)phenyl borate. By using both of these solvent and electrolyte, voltammetry was possible at moderate scan rates with electrodes of millimeter sizes and at faster scan rates with UMEs. About the use of supercritical fluids and ionic liquids as less hazardous media in electrochemistry, it has been discussed previously.

Though various efforts are being made, most promising nonaqueous media for general use in electrochemistry will be nonhazardous or low-hazardous organic solvents (combined with appropriate supporting electrolytes) and nonchloroaluminate ILs. The problem is which of the two to select. An organic solvent may be superior to ILs for one purpose, while an IL may be superior to organic solvents for the other. Here, we should also consider how the wastes of these two should be treated. In the case of organic solvents, they can be evaporated to collect or burnt. On the other hand, ILs can be used repeatedly by washing with water, but the repetition will not be endless. It is fairly difficult to evaporate or burn the ILs, and the problem is how to treat their wastes. Both organic solvents and ILs will be much improved in the future, but it seems that the usefulness of harmless organic solvents will not decrease.

References

- Vitek V (1935) *Collection Czechoslov Chem Commun* 7:537–547
- Riccoboni L, Popoff P (1949) *Gazz Chim Ital* 79:573–587
- Peracchio ES, Meloche VW (1938) *J Am Chem Soc* 60:1770–1775
- Zlotowski I, Kolthoff IM (1942) *J Am Chem Soc* 64:1297–1301
- Shreve OD, Markham EC (1949) *J Am Chem Soc* 71:2993–2997
- Lewis WR, Quackenbush FW, DeVries T (1949) *Anal Chem* 21:762–765
- Wawzonek S, Laitinen HA (1941) *J Am Chem Soc* 63:2341–2343
- Gentry CHR (1946) *Nature* 157:479–480
- Parks TD, Hansen KA (1950) *Anal Chem* 22:1268–1269
- MacGillavry D (1936) *Trans Faraday Soc* 32:1447–1450
- Bachman GB, Astle MJ (1942) *J Am Chem Soc* 64:1303–1309
- Laitinen HA, Wawzonek S (1942) *J Am Chem Soc* 64:1765–1768
- Wawzonek S, Laitinen HA (1942) *J Am Chem Soc* 64:2365–2368
- Pleskov VA (1947) *Usp Khim* 16:254–278
- Grafov BM, Krishtalik LI, Pleskov YuV (2008) *Russ J Electrochem* 44:2–6, Viktor Arturovich Pleskov, On Occasion of His Centenary Jubilee
- Pleskov VA (1948) *Zh Fiz Khim* 22:351–361
- Wawzonek S, Runner ME (1952) *J Electrochem Soc* 99:457–459
- Arthur P, Lyons H (1952) *Anal Chem* 24:1422–1425
- Laitinen HA, Nyman CJ (1948) *J Am Chem Soc* 70:2241–2244, 3002–3008
- Laitinen HA, Shoemaker CE (1950) *J Am Chem Soc* 72:663–665
- Nachtrieb NH, Steinberg M (1948) *J Am Chem Soc* 70:2613–2614
- Lyalikov YuS, Karmazin VI (1948) *Zavodskaya Lab* 14:138–143, 144–148
- Wawzonek S, Blaha EW, Berkey R, Runner ME (1955) *J Electrochem Soc* 102:235–242
- Wawzonek S, Berkey R, Blaha EW, Runner ME (1956) *J Electrochem Soc* 103:456–459
- Hojtink GJ, Van Schooten J, De Boer E, Aalberberg WIJ (1954) *Rec Trav Chim* 73:355–375
- Hojtink GJ (1954) *Rec Trav Chim* 73:895–909
- Hojtink GJ (1955) *Rec Trav Chim* 74:1525–1539
- Austen DEG, Given PH, Ingram DJE, Peover ME (1958) *Nature* 182:1784–1786
- Izutsu K (2009) *Electrochemistry in nonaqueous solutions*, 2nd edn. Wiley-VCH, Weinheim
- Lund H (1957) *Acta Chem Scand* 11:491–498, 1323–1330
- Kolthoff IM, Coetzee JF (1957) *J Am Chem Soc* 79:870–874, 1852–1858
- Coetzee JF, Kolthoff IM (1957) *J Am Chem Soc* 79:6110–6115
- Gutmann V, Schöber G (1959) *Z Anal Chem* 171:339–343
- Strehlow H (1952) *Z Elektrochem* 56:827–833
- Koeppe HM, Wendt H, Strehlow H (1960) *Z Elektrochem* 64:483–491
- Harris WS (1958) *Electrochemical studies in cyclic esters*, Thesis, Report UCRL 8381
- Bruckenstein S, Kolthoff IM (1956) *J Am Chem Soc* 78:2974–2979
- Bruckenstein S, Kolthoff IM (1957) *J Am Chem Soc* 79:5915–5921
- Kolthoff IM, Bruckenstein S (1957) *J Am Chem Soc* 79:1–7
- Maricle DL, Hodgson WG (1965) *Anal Chem* 37:1562–1565
- Peover ME, White BS (1966) *Electrochim Acta* 11:1061–1067
- Johnson L, Pool KH, Hamm RE (1967) *Anal Chem* 39:888–891
- Sawyer DT, Roberts JL Jr (1966) *J Electroanal Chem* 12:90–101
- Fujinaga T, Izutsu K, Adachi T (1969) *Bull Chem Soc Jpn* 42:140–145
- Peover ME, White BS (1967) *J Electroanal Chem* 13:93–99
- Andrieux CP, Hapiot P, Sevéant J-M (1990) *Chem Rev* 90:723
- Butler JN (1970) Reference electrodes in aprotic organic solvents. In: Delahay P, Tobias CW (eds) *Advances in electrochemistry and electrochemical engineering*, vol 7. Interscience, New York, pp 77–175
- Dubois JÉ, Lacaze PC, Ficquelmont AM (1966) *CR Acad Sci Ser C* 262:181–184
- Headridge JB, Pletcher D, Callingham M (1967) *J Chem Soc A* 1967:684–685
- Bréant M, Bazouin M, Buisson C, Dupin M, Rebattu JM (1968) *Bull Soc Chim Fr* 1968:5065–5072
- Kolthoff IM, Chantooni MK Jr (1963) *J Am Chem Soc* 85:426–430
- Kolthoff IM, Chantooni MK Jr (1965) *J Am Chem Soc* 87:1004–1012, 4428–4436
- Kolthoff IM, Chantooni MK Jr (1979) In: Kolthoff IM, Elving PJ (eds) *Treatise on analytical chemistry*, part 1, vol 2, 2nd edn. Interscience, New York, pp 239–302, 349–384
- Jasinski R (1967) *High-energy batteries*. Plenum, New York
- Lund H (2002) *J Electrochem Soc* 149:S21–S33
- Geiger WE (2007) *Organometallics* 26:5738–5765
- Besenhard JO, Eichinger G (1976) *J Electroanal Chem* 68:1–18, 72:1–31
- Ikeda H (1983) In: Gabano J-P (ed) *Lithium batteries*, chapter 8. Academic, London
- Fukuda M, Iijima T (1983) In: Gabano J-P (ed) *Lithium batteries*, chapter 9. Academic, London
- Kanzaki Y, Aoyagui S (1972) *J Electroanal Chem* 36:297–310
- Izutsu K, Sakura S, Kuroki K, Fujinaga T (1971) *J Electroanal Chem* 32:A11–A14
- Izutsu K, Sakura S, Fujinaga T (1972) *Bull Chem Soc Jpn* 45:445–450
- Sleere NV (1976) *J Chem Educ* 53:A12
- Van Duyn RP, Reilley CN (1972) *Anal Chem* 44:142–152, 153–158; 158–169
- Evans DH, Lerke SA (1997) *Electrochemical studies at reduced temperature*. In: Kissinger PT, Heineman WR (eds) *Laboratory techniques in electroanalytical chemistry*, chapter 16, 2nd edn. Marcel Dekker, New York
- Kolthoff IM (1965) *J Polarogr Soc* 10:22–36
- Diggie JW, Parker AJ (1974) *Aust J Chem* 27:1617–1621
- Alfenaar M, DeLigny CL, Remijnse AG (1967) *Rec Trav Chim Pay-Bas* 86:986–992
- Cox BG, Parker AJ, Waghorne WE (1973) *J Am Chem Soc* 95:1010–1014
- Murray RC Jr, Aikens DK (1976) *Electrochim Acta* 21:1045–1053
- Senanayake G, Muir DM (1987) *J Electroanal Chem* 237:149–162
- Kahanda C, Popovych O (1994) *Aust J Chem* 47:921–931, and references therein
- Izutsu K, Nakamura T, Kitano T, Hirasawa C (1978) *Bull Chem Soc Jpn* 51:783–789
- Izutsu K (1998) *Pure Appl Chem* 70:1873–1880 (short review)
- Izutsu K, Kobayashi N (2005) *J Electroanal Chem* 574:197–206
- Izutsu K (2010) *Bull Chem Soc Jpn* 83:777–781
- Gale RJ, Gilbert B, Osteryoung RA (1978) *Inorg Chem* 17:2728–2729
- Gale RJ, Osteryoung RA (1979) *Inorg Chem* 18:1603–1605
- Gale RJ, Gilbert B, Osteryoung RA (1979) *Inorg Chem* 18:2723–2725
- Robinson J, Osteryoung RA (1979) *J Am Chem Soc* 101:323–327
- Ohno H (ed) (2005) *Electrochemical aspects of ionic liquids*. Wiley, New York
- Wasserscheid P, Welton T (eds) (2008) *Ionic liquids in synthesis*, vols. 1 & 2, 2nd edn. Wiley-VCH, Weinheim
- Endres F, MacFarlane D, Abbott D (eds) (2008) *Electrodeposition from ionic liquids*. Wiley-VCH, Weinheim
- Gavach C, Henry F (1974) *J Electroanal Chem* 54:361–370

85. Gavach C, D'Epenoux B (1974) *J Electroanal Chem* 55:59–67
86. Gavach C, D'Epenoux B, Henry F (1975) *J Electroanal Chem* 64:107–115
87. Koryta J, Vanýsek P, Březina M (1976) *J Electroanal Chem* 67:263–266
88. Koryta J, Vanýsek P, Březina M (1977) *J Electroanal Chem* 75:211–228
89. Samek Z, Mareček V, Koryta J, Khalil MW (1977) *J Electroanal Chem* 83:393–397
90. Davies PW, Brink F (1942) *Rev Sci Instrum* 13:524–533; Clark LC Jr, Wolf R, Granger D, Taylor Z (1953) *J Appl Physiol* 6:189–193
91. Clark LC Jr, Wolf R, Granger D, Taylor Z (1953) *J Appl Physiol* 6:189–193
92. Amatore C (1995) Electrochemistry at ultramicroelectrodes. In: Rubinstein I (ed) *Physical electrochemistry, principles, methods, and applications*, chapter 4. Marcel Dekker, New York
93. Michael AC, Wightman RM (1996) Microelectrodes. In: Kissinger PT, Heineman WR (eds) *Laboratory techniques in electroanalytical chemistry*, chapter 12, 2nd edn. Marcel Dekker, New York
94. Penner RM, Herben MJ, Longin TL, Lewis NS (1990) *Science* 250:1118–1121
95. Clegg AD, Rees NV, Klymenko OV, Coles BA, Compton RG (2005) *J Electroanal Chem* 580:78–86
96. Silvestri G, Gambino S, Filardo G, Cuccia C, Guarino E (1981) *Angew Chem Int Ed* 20:101–102
97. McDonald AC, Fan FRF, Bard AJ (1986) *J Phys Chem* 90:196–202
98. Flarsheim WM, Tsou YM, Trachtenberg I, Johnston KP, Bard AJ (1986) *J Phys Chem* 90:3857–3862
99. Flarsheim WM, Bard AJ, Johnston KP (1989) *J Phys Chem* 93:4234–4242
100. Liu CY, Snyder SR, Bard AJ (1997) *J Phys Chem B* 101:1180–1185
101. Crooks RM, Fan FRF, Bard AJ (1984) *J Am Chem Soc* 106:6851–6852
102. Crooks RM, Bard AJ (1988) *J Electroanal Chem* 243:117–131
103. Cabrera CR, Garcia E, Bard AJ (1989) *J Electroanal Chem* 260:457–460
104. Niehaus D, Philips M, Michael A, Wightman RM (1989) *J Phys Chem* 93:6232–6236
105. Li J, Prentice G (1997) *J Electrochem Soc* 144:4284–4288
106. Olsen SA, Tallman DE (1994) *Anal Chem* 66:503–509
107. Olsen SA, Tallman DE (1996) *Anal Chem* 68:2054–2061
108. Krishtalik LI, Alpatova NM, Ovsyannikova EV (1991) *Electrochim Acta* 36:435
109. Abbott AP, Eardley CA, Harper JC, Hope EG (1998) *J Electroanal Chem* 457:1–4
110. Gritzner G, Kuta J (1984) *Pure Appl Chem* 56:461–466
111. Mussini T, Covington AK, Longhi P, Rondinini S (1985) *Pure Appl Chem* 57:865–876; for new recommendation, see Rondinini S (2002) *Anal Bioanal Chem* 374:813–816
112. Coetzee JF (1982) *Recommended methods for purification of solvents and tests for impurities*. Pergamon, Oxford, For other reports, see Section 10.4 of [29]
113. Izutsu K (1990) Acid-base dissociation constants in dipolar aprotic solvents, IUPAC Chemical Data Series No. 35. Blackwell Science, Oxford
114. Yoshino M, Brodd RJ, Kozawa A (eds) (2009) *Lithium-ion batteries: science and technologies*. Springer, New York
115. Weaver MJ (1992) *Chem Rev* 92:463–480
116. Galus Z (1995) Electrochemical reactions in nonaqueous and mixed solvents. In: Gerischer H, Tobias CW (eds) *Advances in electrochemical science and engineering*, vol 4. VCH, Weinheim, pp 217–295
117. Miller CJ (1995) Heterogeneous electron transfer kinetics at metallic electrodes. In: Rubinstein I (ed) *Physical electrochemistry, principles, methods and applications*, chapter 2. Marcel Dekker, New York
118. Echegoyen L, Echegoyen LE (1998) *Acc Chem Res* 31:593–601
119. Echegoyen LE, Herranz MA, Echegoyen L (2006) Fullerenes. In: Scholz F, Pickett CJ (eds) *Bard-Stratmann encyclopedia of electrochemistry*, vol 7a, inorganic chemistry. Wiley-VCH, Weinheim, pp 145–201
120. Oyama M, Nozaki K, Nagaoka T, Okazaki S (1990) *Bull Chem Soc Jpn* 63:33–41
121. Oyama M, Higuchi T, Okazaki S (2000) *Electrochem Commun* 2:675–678
122. Izutsu K, Nakamura T, Hiraoka S (1993) *Chem Lett* 1843–1846
123. Izutsu K, Ohmaki M (1995) *Talanta* 43:643–648
124. Wilkes JS, Zaworotko MJ (1992) *J Chem Soc, Chem Commun* 1992:965–967
125. Ranke J, Stolte S, Störmann R, Arning J, Jastorff B (2007) *Chem Rev* 107:2183–2206
126. Xu K (2004) *Chem Rev* 104:4303–4418
127. Conway BE (1999) *Electrochemical superconductors, scientific fundamentals and technological applications*. Kluwer Academic/Plenum Publishers, New York
128. Ue M (2007) *Electrochemistry* 75:565–572
129. Ue M (2005) Chapter 17 of [81]
130. Amatucci GG, Badway F, Pasquier AD, Zhang T (2001) *J Electrochem Soc* 148:A930–A939
131. Yoshio M, Nakamura H, Wang H (2006) *Electrochem Solid-State Lett* 9:A561–A563
132. Yoshizumi A, Uehara A, Kasuno M, Kitatsuji Y, Yoshida Z, Kihara S (2005) *J Electroanal Chem* 581:275–283
133. Kakiuchi T (2007) *Anal Chem* 79:6442–6449
134. Kakiuchi T (2008) *Anal Sci* 24:1221–1230
135. Kakiuchi T, Yoshimatsu T (2006) *Bull Chem Soc Jpn* 79:1017–1024
136. Kakiuchi T, Yoshimatsu T, Nishi N (2007) *Anal Chem* 79:7187–7191
137. Scholz F, Komorsky-Lovric S, Lovric M (2000) *Electrochem Commun* 2:112–118
138. Banks CE, Davies TJ, Evans RG, Hignett G, Wain AJ, Lawrence NS, Wadhawan JD, Marken F, Compton RG (2003) *Phys Chem Chem Phys* 5:4053–4069
139. Scholz F, Gulaboski R (2005) *ChemPhysChem* 6:16–28
140. Bak E, Donten M, Stojek Z (2007) *J Electroanal Chem* 600:45–53
141. Donten M, Bak E, Gniadek M, Stojek Z, Scholz F (2008) *Electrochim Acta* 53:5608–5614
142. Anastas PT (2002) Green chemistry as applied to solvents. In: Abraham MA, Moens L (eds) *Clean solvents: alternative media for chemical reactions and processing*, chapter 1. Oxford Univ Press, Oxford
143. LeSuer RJ, Geiger WE (2006) *J Electroanal Chem* 594:20–26
144. Ovenall DW, Whiffen DH (1958) Electron spin resonance measurements on some organosodium complexes, Chemical Society Symposium, Electron and Nuclear Magnetic Resonance, Bristol