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Conference Paper

Electrochemical Generation of Solvated Electrons and Hydrogen Evolution in Hexamethylphosphortriamide*

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Electrolysis experiments with rotating disc electrodes of copper, amalgamated copper, and platinum in anhydrous hexamethylphosphortriamide are described. It is shown that the generation of solvated electrons is a primary process. In the same solutions (0.2 M LiCl + 0.09 to 0.20 M HCl) hydrogen evolution occurs as a direct proton discharge step and not through a reaction with the solvated electron(s).

Electrochemical generation of solvated electrons is a special, scantily studied, class of electrochemical reactions. In media in which the stability of solvated electrons is high enough, the process of their generation may be relatively easily studied. This study is of interest in several aspects.

First, this process is a convenient method to obtain electrons in the bulk of solution. This affords information on the properties of electrons in the condensed phase.

Second, this study gives us possibility to establish the mechanism of the generation process itself.

Third, by comparing the regularities of generation with those of common electrochemical reactions, we can obtain knowledge of the elementary act mechanism of an electrochemical process. A number of investigators¹⁻⁵ suggested that many electrochemical reactions and processes of spontaneous dissolution of metals pass through an intermediate stage of solvated electron formation. The possibility of such a mechanism and the arguments adduced by above authors were questioned by other investigators⁶⁻⁹. The object of our study was direct experimental comparison of the two mechanisms: the direct discharge of ions and their reaction with solvated electrons.

As the subject of our study we chose anhydrous solutions of LiCl in hexamethylphosphortriamide (0.2 mole/l). Earlier one of the authors together with A. D. Grishina showed¹⁰ that the ESR spectrum of the solvated electron generated electrochemically in LiCl solutions is characterized by a single narrow line. The line width does not depend on the electron concentration, the aggregate state and temperature. This led us to suggest that the small

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line width of the ESR spectrum is due to high symmetry of the electron solvation sheath. The solvated electron interacts weakly with salt cations.

Electrochemical measurements¹¹ were performed at 25°. Lead immersed in LiCl solution (0.2 mole/l) with PbCl₂ addition (0.01 mole/l) was used as a reference electrode. Its potential *versus* N. H. E. in hexamethylphosphor-triamide is about -0.50 ± 0.01 v.

The polarization curves were plotted under galvanostatic conditions on stationary and rotating disc electrodes from copper, amalgamated copper, platinum and gallium. In the case of neutral lithium chloride solutions, the measurements on an electropolished copper electrode showed the best reproducibility.

Stirring either has no effect or, in the presence of water traces, causes passivation. This passivation can be associated with formation of difficultly soluble basic lithium compounds. Pre-electrolysis of unstirred solution eliminates the traces of water near the cathode and the passivation is avoided. The enrichment with electrons of the layer adjacent to the cathode enhances its conductivity and makes the ohmic drop negligible.

A characteristic polarization curve obtained on a copper electrode in LiCl solution is shown in Fig. 1, Curve 1. The region of the scatter of

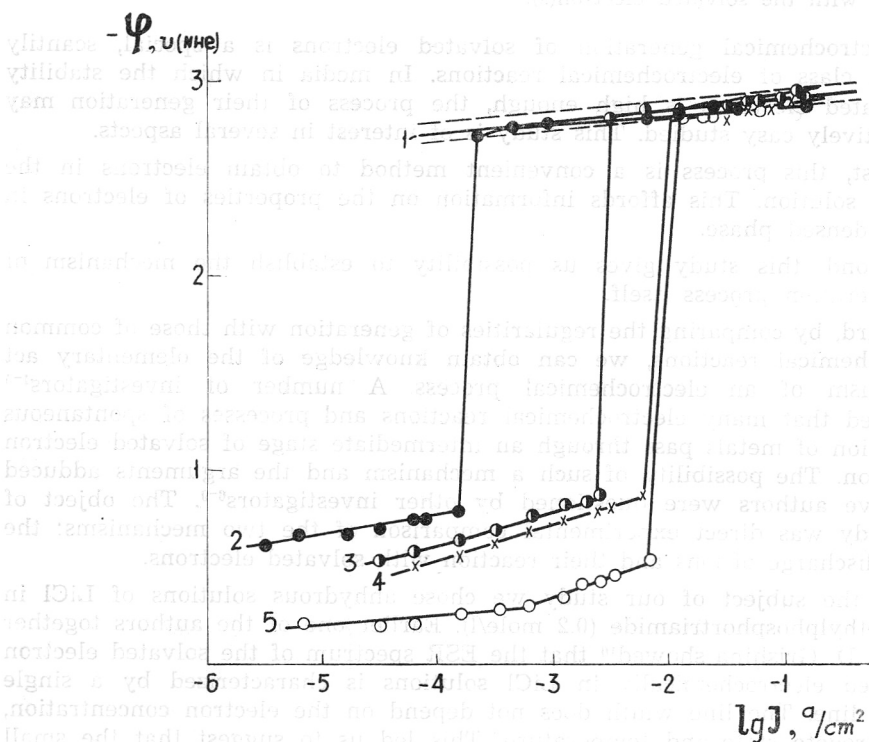


Fig. 1. Dependence of the potential ϕ , v (N.H.E.) on the current density I , a/cm² at 25°C in LiCl solution (0.2 mole/l) in hexamethylphosphor-triamide with HCl additions. 1 — without HCl, 2 — 0.09 mole/l, 3 — 0.15 mole/l, 4 — 0.24 mole/l, 5 — 0.20 mole/l. Electrode material: 1-4 — copper, 5 — platinum.

experimental data for different series of experiments in different solvent lots is confined within dotted lines. For one lot the scatter is much less.

It can be seen that within a wide current range the curve is described by the Tafel slope of 60 mv. This shape of the curve can be attributed to various mechanisms.

First, to the concentration polarization associated with the removal of the reaction product.

Second, to lithium electrodeposition, followed by its dissolution. Like liquid ammonia, hexamethylphosphortriamide can dissolve alkali metals with formation of solvated electrons.

The third mechanism corresponding to the shape of the polarization curve obtained is thermal emission.

The fourth mechanism is electrochemical dissolution according to the barrierless mechanism with formation of electrons localized near the electrode.

The hypothesis about the concentration polarization is at variance with the absence of the potential shift in the positive direction with increased stirring rate.

In all probability, lithium electrodeposition should be accompanied by the appearance of the limiting current of lithium ions diffusion at low lithium salt concentrations. This limiting current is actually observed on an amalgamated copper disc electrode as amalgam is formed. Its diffusion-migration nature is proved by the dependence of the limiting current on the rotation rate and lithium chloride concentration (Fig. 2).

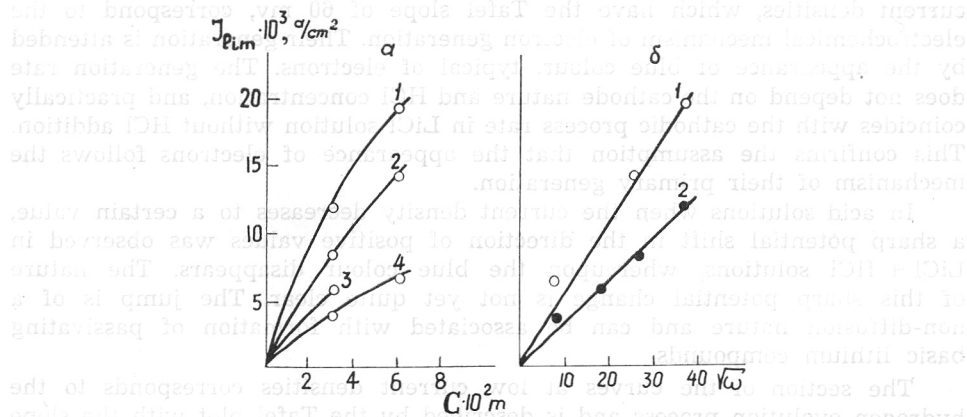


Fig. 2. a) Dependence of the limiting diffusion-migration current I_{lim} , a/cm² on an amalgamated copper electrode on lithium chloride concentration C mole/l, 1 — 1340 rpm, 2 — 670 rpm, 3 — 380 rpm, 4 — 64 rpm. b) Dependence of the limiting diffusion-migration current I_{lim} , a/cm² on an amalgamated copper electrode on the rotation rate ω , rpm, 25°. 1 — 0.061 mole/l, 2 — 0.031 mole/l.

On a copper electrode in diluted lithium chloride solutions the limiting currents are absent at the values higher than expected. This fact, as well as the current rise after the limiting current, accompanied by the appearance of blue colour, observed on the amalgamated electrode, suggest that the generation of solvated electrons is not associated with lithium electrodeposition and its subsequent dissolution, but is a primary process. The most likely mechanism of this process would be thermal emission. The

barrierless electrochemical dissolution with increasing current density should pass into the common process, altering the polarization curve slope to 120 mv. This was not observed. However to make a final choice between these two mechanisms it is necessary to get additional experimental data.

Thus, the results obtained indicate the primary nature of generation of solvated electrons. The regularities of this process can be used in considering the mechanism of hydrogen evolution. For this purpose, polarization measurements were carried out in LiCl solutions with HCl additions on copper and platinum electrodes (Fig. 1, Curves 2—5).

In lithium chloride solutions without HCl additions no reproducible results could be obtained on platinum and solid gallium electrodes. This is, probably, due to the penetration of the alkali metal into the electrode. In solutions with HCl additions satisfactory reproducibility was obtained also on the platinum electrode as well, owing, probably, to suppression of this penetration.

In 1935 Frumkin proved theoretically that the rate of any electrochemical reaction does not depend directly on the work function of the metal-vacuum system. At a given potential the work function from any metal into solution is the same. For photoemission into solution this conclusion was confirmed by Rotenberg and Pleskov¹². This thesis should also hold for electron generation both by the thermal emission and the electrochemical dissolution mechanisms.

In LiCl + HCl solutions the sections of the polarization curves at high current densities, which have the Tafel slope of 60 mv, correspond to the electrochemical mechanism of electron generation. Their generation is attended by the appearance of blue colour, typical of electrons. The generation rate does not depend on the cathode nature and HCl concentration, and practically coincides with the cathodic process rate in LiCl solution without HCl addition. This confirms the assumption that the appearance of electrons follows the mechanism of their primary generation.

In acid solutions when the current density decreases to a certain value, a sharp potential shift in the direction of positive values was observed in LiCl + HCl solutions, whereupon the blue colour disappears. The nature of this sharp potential change is not yet quite clear. The jump is of a non-diffusion nature and can be associated with formation of passivating basic lithium compounds.

The section of the curves at low current densities corresponds to the hydrogen evolution process and is described by the Tafel plot with the slope 120—140 mv for copper and 60—140 mv for platinum. The hydrogen evolution rate depends on the cathode nature and acid concentration in a manner, on the whole, similar to an aqueous solution.

As is clear from Fig. 1 the electron generation potentials are displaced relative to the hydrogen evolution potentials in the cathodic direction by about 2 v. This indicates that the hydrogen evolution process is a primary one and is not associated with the interaction of proton donors and solvated electrons.

Of course, when passing to other solvents, the energetics of ions and electrons can change, but it is hardly probable that these changes should exceed 2 v. At any rate, for acid solutions it can be assumed that hydrogen

evolution does not pass through the stage of formation of solvated electrons. For alkaline solutions the direct discharge of water molecules is the more likely mechanism too.

The difference of 2 v is much larger than the potential difference of hydrogen evolution from acid and alkaline solutions. Moreover, hydrogen evolution from alkaline solutions and electron generation are characterized by different slopes of the polarization curves (120 and 60 mv).

Thus, these studies have shown that:

1. Generation of solvated electrons is a primary process.
2. Hydrogen evolution, at least from acid solutions, occurs as a direct proton donor discharge, rather than by way of reaction with solvated electrons.

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IZVOD

Elektrokemijsko stvaranje solvativiranih elektrona i razvijanje vodika u heksametilfosfortriamidu

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Opisani su eksperimenti elektrolize u heksametilfosfortriamidu (HMPT), otapalu za koje je poznato da izuzetno dobro stabilizira solvativirane elektrone. Mjerene su krivulje polarizacije za rotirajuće disk elektrode od bakra, amalgamiranog bakra i platine. Pokazano je da se Tafelovi pravci, dobiveni za bakar i platinu u otopinama $\text{LiCl} + \text{HCl}$ u HMPT, mogu podijeliti u dvije grupe: jedni, mjereni ispod -1.0 V prema normalnoj vodikovoj elektrodi u istom mediju s nagibom od oko 120 mV/log gustoće struje posljedica su reakcije razvijanja vodika, i to direktnim izbojem protona; drugi, mjereni kod potencijala oko $-2,6$ do $-2,8$ V, uzrokovani su stvaranjem solvativiranih elektrona, i to jednim primarnim procesom.

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