

Effects of Electric Field in Contact Glow Discharge Electrolysis of Acetonitrile Solution

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The chemical reactions brought about in acetonitrile solution by means of contact glow discharge electrolysis (cgde) were studied. A steady discharge could be sustained around a platinum wire anode in contact with the surface of solution, when dc high voltage over 400V was applied between the anode and cathode of SUS plate submerged in the solution under argon atmosphere. As major products, propionitrile, succinonitrile, and acrylonitrile were obtained in the solution. The amounts of products exceeded the limit on basis of Faraday's law and rapidly grew up with the higher applied voltage. When the polarity of electrodes was reversed, the voltage above 350V was required to sustain the steady discharge around the cathode. There were found fumaronitrile and maleonitrile as the additional products. In contrast with the case of anodic discharge, the amounts of products were independent of the applied voltage, although they were still beyond the above-mentioned limit. The difference between anodic and cathodic discharge might be primarily attributed to that of the chemical behavior of reactive species initiating the solution-phase reactions, that is, the cation and electron in anodic and cathodic cgde, respectively.

Key words: Glow discharge electrolysis, Ambient pressure plasma, Electric field effect, Acetonitrile solution, Radical recombination

1. INTRODUCTION

When a thin wire electrode is in contact with the surface of electrolytic solution and an auxiliary one is submerged in the solution, one can generate the discharge around the wire electrode by applying dc high voltage between the electrodes. The dc current flows through the glow discharge and the charged species accelerated due to the potential gradient in the discharge rush against the surface of electrolyte with considerable magnitude of kinetic energy to bring about chemical changes in the solution. This phenomenon was termed contact glow discharge electrolysis (cgde).¹⁻³⁾ There have been a number of studies regarding the chemical effects yielded on either inorganic or organic substances in aqueous solutions by means of cgde.^{1-5, 14)} The oxidative degradation of a variety of amino and carboxylic acids was intensively investigated in the relevance to chemical evolution.⁶⁻¹³⁾ In the earlier works, authors have undertaken to apply the cgde technique to the treatment of waste water, too.¹⁵⁻¹⁸⁾ On the other hand, to our knowledge, less attention has been devoted to the cgde of nonaqueous solutions except for methanol.¹⁹⁾

Recently, the preliminary results on the chemical effects caused by cgde of acetonitrile solution were reported.²⁰⁾ In the present paper, we focus on the influence of the polarity of discharge electrode on the reaction pathway in association with the reactive species responsible for the initiation step in the liquid-phase.

2. EXPERIMENTAL

The electrolytic cell employed in cgde experiments is schematically drawn in Fig. 1. The two compartments were separated by a sintered glass disk of medium

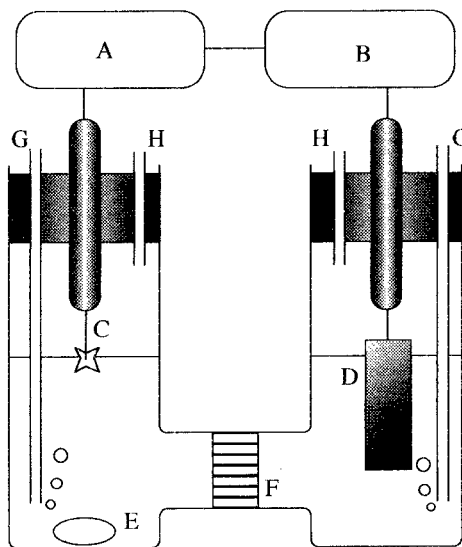


Fig 1. Electrolytic cell for cgde of acetonitrile solution

A: dc power source, B: digital coulomb-meter,
C: Pt wire, D: SUS plate, E: magnet bar,
F: sintered glass disk, G: gas inlet, H: gas outlet

porosity from each other. The electrode, from which the discharge was emitted, was a pointed platinum wire (i.d. 0.6 mm) sealed into a glass tube. A stainless steel plate was used as an auxiliary electrode. Acetonitrile solution containing 0.1 M of lithium perchlorate as a supporting electrolyte was placed in the cell, through which argon was passed to purge air. The wire electrode was dipped into the solution by the depth of approximately 1 mm. To start cgde, the high voltage was supplied from a dc

power source, which could provide the current up to 0.1 A at the voltage of 0-1500 V. During the electrolysis, the cell was immersed in an ice-water bath and the solution was gently stirred by means of magnet bar. A digital coulomb-meter was used to determine the electricity passed in the experiments. The electrolysis products were analyzed by gas chromatography and mass spectrometry. Capillary columns used were PEG-20M and OV-1 bonded. The solvent and supporting electrolytes were commonly purified prior to use.

3. RESULTS AND DISCUSSION

Whether the discharge electrode is an anode or cathode, one can perform cgde experiments using acetonitrile solution, if a supporting electrolyte is chosen appropriately so that it may afford the sufficient conductance to the solution.

3.1 Anodic cgde

Figure 2 shows the typical current-voltage relationship in cgde of acetonitrile solution, where the discharge electrode and supporting electrolyte were the anode and lithium perchlorate, respectively. It falls into several sections. In the linear section below 100V, Ohm's law was obeyed and the conventional electrolysis proceeded with small bubbles of gas leaving the wire anode. At 100V, the smooth evolution of bubbles was interrupted and the small flashes of light were seen at the anode. Between 100V and 300V, the readings of both current and voltage fluctuated wildly and the intermittent discharge was observed. In the neighborhood of 300V, the readings of current and voltage were suddenly stabilized. The flow of bubbles from the anode surface had now ceased and appeared to have been replaced by a smooth pale sheath of vapor. Above the voltage of 400V, the continuous reddish violet glow became apparent. This might be taken as a true cgde region. The intensity of light emission

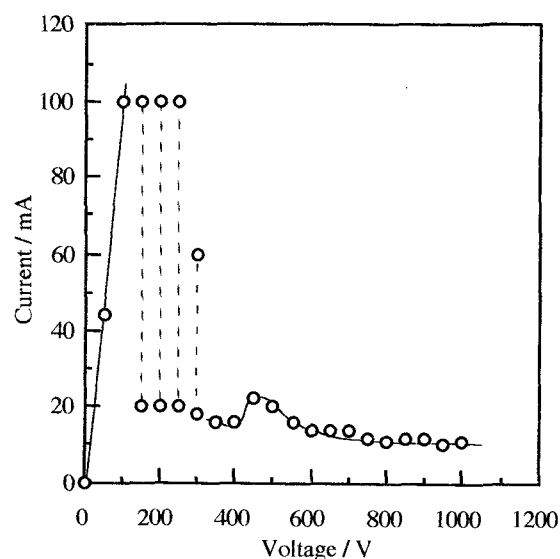


Fig 2. Current-voltage relationship in anodic cgde of 0.1M LiClO₄-acetonitrile

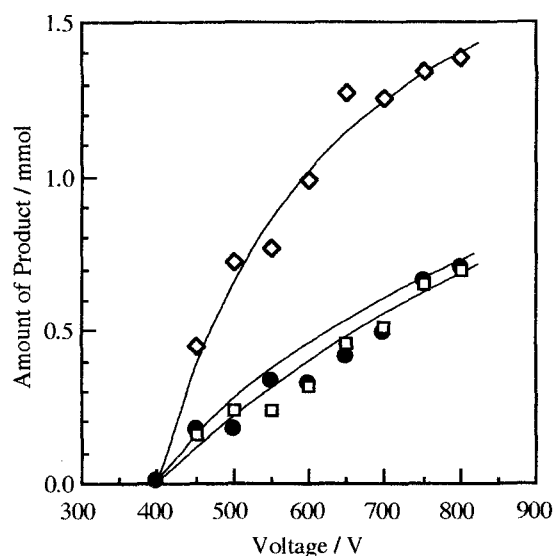


Fig 3. Effect of voltage on products in anodic cgde of 0.1M LiClO₄-acetonitrile
electricity: 30C, (◇)PN, (□)AN, (●)SN

increased with rising voltage, while the current was substantially unchanged up to 1000 V. A hump was reproducibly observed in the beginning of this region, but the origin was obscure so far. These characteristics were quite similar to those observed in cgde of aqueous solutions, except that the discharge current had ascent monotonously with higher voltage.^{1,3)}

The major products obtained in the solution-phase were propionitrile(PN), succinonitrile(SN), and acrylonitrile(AN). The last might be most likely to be derived through the secondary reactions of PN under the condition. In the gas sampled out through the gas outlet of the cell in the course of cgde, methane, ethane, ethylene and acetylene were detected as well as hydrogen cyanide and cyanogen. These gaseous products, however, were not further quantified. The effects of applied voltage on the amounts of PN, SN, and AN are demonstrated in Fig. 3, where each run was discontinued at constant electricity of 30C. It was evident that these products were substantially formed only in the region of true cgde as mentioned above. More interesting results are concerning to the amounts of products. The maximum of gross amounts should have been approximately 0.15 mmol for 30C of electricity if one assumed that the Faraday's law held in the present system and two electron oxidation process would be required for the formation of these products. In practice, they exceeded the limit around the voltage of 500V and totally amounted to 1.2mmol. Besides, they rose steeply with the increase in voltage. These facts indicate that the chemical changes occurring in the course of cgde are quite different from those in a classical electrolysis, where Faraday' law is strictly obeyed. The effects of electricity passed on the product amounts obtained in anodic cgde at 500V of applied voltage are exhibited in Fig. 4. As expected, the amounts proportionally accumulated in the solution as

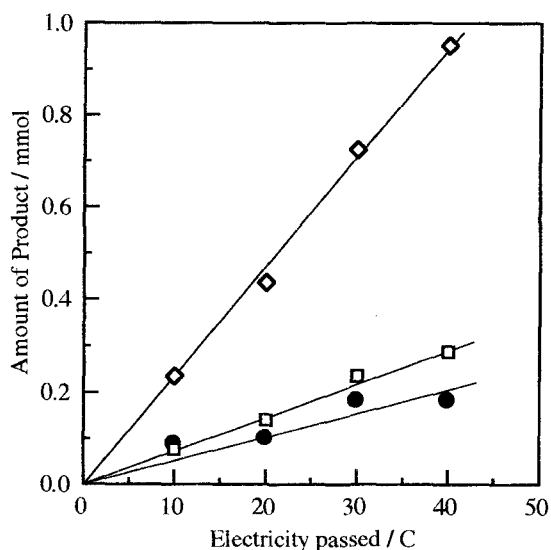


Fig 4. Effect of electricity passed on products in anodic cgde of 0.1M LiClO₄-acetonitrile applied voltage: 500V, (◇)PN, (□)AN, (●)SN

the electrolysis was continued up to the electricity of 40C.

3.2 Cathodic cgde

When the discharge electrode was switched to cathode from anode, the voltage above 350V was required to sustain the steady discharge around the cathode. The current-voltage relationship in cathodic cgde of acetonitrile solution was displayed in Fig. 5. The visual appearance was basically similar to that in anodic cgde up to 600V. With higher voltage, the current continued to move upward and finally drove Pt wire electrode to melt.

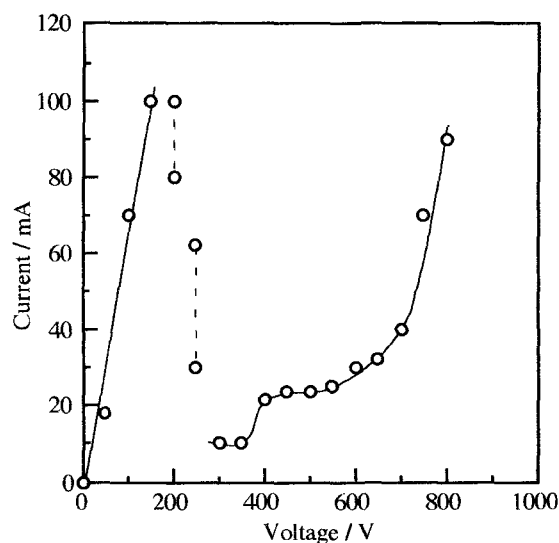


Fig 5. Current-voltage relationship in cathodic cgde of 0.1M LiClO₄-acetonitrile

Also in cathodic cgde, PN, SN, and AN were given as major products. Furthermore, there were found fumaronitrile(FN) as the additional product as well as a trace amount of maleonitrile(MN). It seems convincing that the latter two should result from the overconversion of SN. As seen in Fig. 6, the amounts of these products increased linearly with the duration of electrolysis, similarly in anodic cgde, although the rates were considerably lowered. In contrast, Fig. 7 revealed that the dependence on the applied voltage was diverse from that in anodic cgde. The amounts of products were unaffected by the applied voltage when the electricity was maintained at constant value.

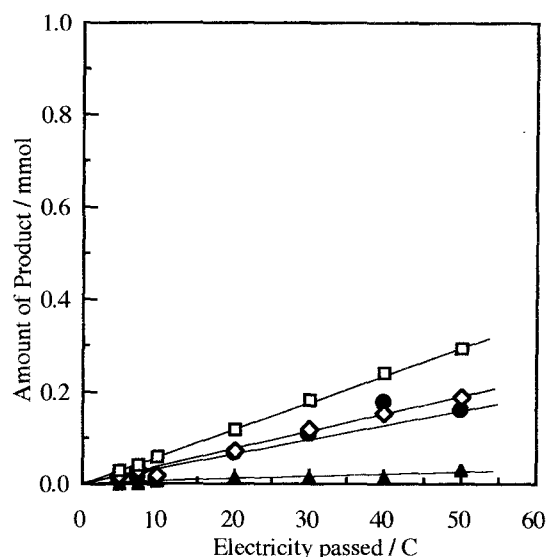


Fig 6. Effect of electricity passed on products in cathodic cgde of 0.1M LiClO₄-acetonitrile applied voltage: 500V, (◇)PN, (□)AN, (●)SN, (▲)FN

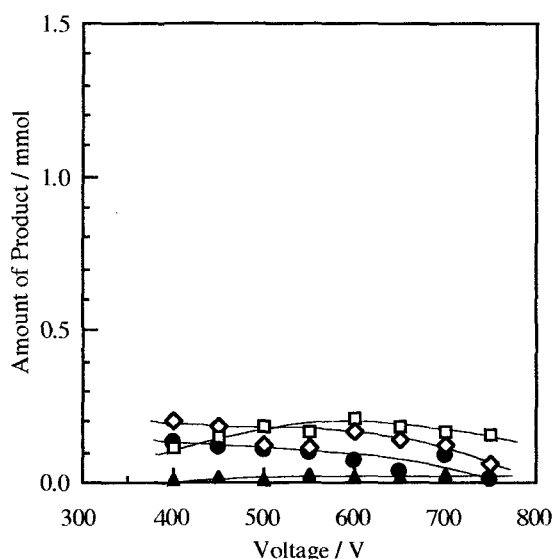


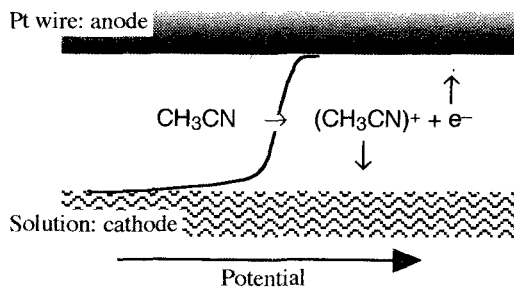
Fig 7. Effect of voltage on products in cathodic cgde of 0.1M LiClO₄-acetonitrile electricity: 30C, (◇)PN, (□)AN, (●)SN, (▲)FN

3.3 Polarity effects

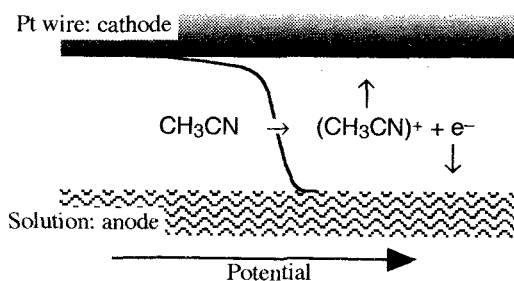
Taking account of the results stated previously, the following scheme might be the most plausible in cgde of acetonitrile: 1) acetonitrile molecule would be ionized in the plasma region; 2) the charged species might be accelerated according to the potential gradient in the discharge zone and bombard one or more acetonitrile molecules existing in the vicinity of solution surface to give rise to the subsequent bond cleavage in the target molecules; 3) the resulting radicals could recombine mutually to lead to the aforesaid products.

The difference between anodic and cathodic cgde might be primarily attributed to that of the chemical behavior of reactive species initiating the solution-phase reactions, that is, the cation and electron in anodic and cathodic cgde, respectively. Moreover, the magnitude of kinetic energy which the charged species would acquire until they reached the solution surface might crucially depend on its polarity. It is taken for granted that the distribution of potential in dc glow discharge is uneven and the gradient in the vicinity of cathode, so-called cathode fall, is remarkably large in compared with that imposed on anode. Therefore, in anodic cgde, where the surface of solution may be regarded to function as the cathode of gaseous discharge, the cation can get much more accelerating energy than that of electron in cathodic cgde. This situation is intelligibly illustrated in Scheme 1. In addition, the increase in the applied voltage might be mostly contributed to the increment in cathode fall. It seems that such ideas can explain the experimental results the most consistently.

1) Anodic cgde



2) Cathodic cgde



Scheme 1. Charged Species and potential gradient in anodic and cathodic cgde

Further study is progressing to elucidate the reaction mechanism and exploit the synthetic application of cgde.

Acknowledgement

Financial support from Grant-in-Aid for Scientific Research(11450337) of The Ministry of Education, Science, Sports, and Culture of Japan, and High-Tech Research Center of Saitama Institute of Technology is acknowledged.

References

- 1) A. Hickling and M. D. Ingram, *J. Electroanal. Chem.*, **8**, 65-81 (1964).
- 2) A. Hickling, "Modern Aspects of Electrochemistry", Ed. by J. O'M. Bocklis and B. E. Conway, Vol. 1, Plenum Press, New York, NY(1971) pp. 329-373.
- 3) A. Hickling and M. D. Ingram, *Trans. Faraday Soc.*, **60**, 783-793 (1964).
- 4) A. R. Denaro and K. O. Hough, *Electrochim. Acta*, **17**, 549-559 (1972).
- 5) M. A. Almubarak and A. Wood, *J. Electrochem. Soc.*, **124**, 1356-1360 (1977).
- 6) K. Harada and T. Iwasaki, *Nature*, **250**, 426-428 (1974).
- 7) K. Harada and T. Iwasaki, *Chem. Lett.*, **1975**, 185-188.
- 8) J. Terasawa and K. Harada, *Chem. Lett.*, **1980**, 73-76.
- 9) K. Harada and J. Terasawa, *Chem. Lett.*, **1980**, 441-444.
- 10) K. Harada, J. Terasawa, and H. Gunji, *Chem. Lett.*, **1980**, 1545-1548.
- 11) E. Kokufuta, T. Sodeyama, K. Fujimori, K. Harada, and I. Nakamura, *J. Chem. Soc., Chem. Commun.*, **1984**, 269-270.
- 12) E. Kokufuta, T. Shibasaki, I. Nakamura, K. Harada, and T. Sodeyama, *J. Chem. Soc., Chem. Commun.*, **1985**, 100-102.
- 13) K. Harada, S. Igari, M. Takasaki, and A. Shimoyama, *J. Chem. Soc., Chem. Commun.*, **1986**, 1384-1385.
- 14) S. K. Sengupta, A. K. Srivastava, and R. Singh, *J. Electroanal. Chem.*, **427**, 23-27 (1997).
- 15) M. Tezuka, *Denki Kagaku* (presently *Electrochemistry*), **61**, 794-795 (1993).
- 16) M. Tezuka and M. Iwasaki, *Denki Kagaku* (presently *Electrochemistry*), **65**, 1057-1060 (1997).
- 17) M. Tezuka and M. Iwasaki, *Thin Solid Films*, **316**, 123-127 (1998).
- 18) M. Tezuka and M. Iwasaki, *Plasmas & Ions*, **2**, 23-26 (1999).
- 19) G-A. Mazzocchin, G. Bontempelli, and F. Magno, *J. Electroanal. Chem.*, **42**, 243-252 (1973).
- 20) M. Tezuka and M. Iwasaki, submitted.