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Electrochemical Fixation of Molecular Nitrogen on p-Type Gallium Phosphide Photocathode

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Electrochemical fixation of molecular nitrogen to ammonia and hydrazine at p-type GaP photocathodes was studied in nonaqueous electrolytes containing either one of titanium tetraisopropoxide, titanium trichloride, vanadium trichloride, or chromium trichloride and a trace amount of water. Positive evidences for the nitrogen fixation were obtained in these electrolytes, but the current efficiency was quite low, and usually less than 1%. It is suggested from the present study that there are a variety of choices of electrolyte systems for the nitrogen fixation.

The fixation of molecular nitrogen to ammonia and hydrazine under mild ambient conditions has been an important subject in chemical research fields. The most intensive studies have been done on nitrogen fixation *via* nitrogen complexes, which are summarized in a recent review.[1]

The fixation of N_2 by a photoelectrochemical process was reported in 1978 by Dickson and Nozik,[2] who used an electrolyte system reported by Van Tamelen and his coworkers,[3-5] *i.e.*, titanium tetraisopropoxide in 1,2-dimethoxyethane(glyme) which was originated from previous studies on nitrogen fixation *via* nitrogen metallo-organic complexes.[3] An essential component of the electrolyte is judged to be titanium tetraisopropoxide which can bind and ionize N_2 when reduced to a divalent species in the course of the electrolysis. Electrochemical fixation of N_2 was also reported to be possible if N_2 is subjected to a silent discharge prior to bubbling into aqueous electrolytes of sulfuric acid or potassium hydroxide,[6] but this approach should be excluded from nitrogen fixation under mild conditions.

It is known from redox potentials of $Ti^{3+/4+}$ and $Ti^{2+/0}$ in aqueous solutions[7] that Ti(II) is a strong reducing agent. The Ti(II) species originated from titanium tetraisopropoxide in glyme must also have a high reducing power. The idea has then developed that from an electrochemical point of view the chemical species having a reducing power comparable to that of the Ti(II) species may work effectively to fix N_2. We tested Cr(II), V(II) as well as Ti(II), and found that nitrogen fixation is possible on illuminated p-type GaP cathodes with assistance of these reducing agents. Although obtained current efficiencies for the nitrogen fixation were very low, the results obtained in the present study suggested that there are a variety of choices of solvent-electrolyte systems to fix N_2 by the photoelectrochemical process.

Experimental

1,2-Dimethoxyethane (glyme), propyrene carbonate (PC), methanol, acetonitrile, and *N,N*-dimethylformide (DMF) were chosen as the solvent of electrolytes into which $AlCl_3$ as an indifferent electrolyte and either one of the redox agents, $Ti[OCH(CH_3)_2]_4$, $TiCl_3$, VCl_3, or $CrCl_3$ were dissolved. In the case $CrCl_3$, $CrCl_2$ was also dissolved in a small amount to raise its solubility. We arbitrarily chose the concentration of the redox agent to be 10 mmol per 50 ml of the solvent. However, the solubility was often found to be too low to satisfy this standard, necessitating the use of a much lower concentration. The solubility of $AlCl_3$ was also often too low in the presence of the redox agents of the chloride form to dissolve 15 mmol to 50 ml of the redox solutions. Among the solvents used, PC, with which major experiments of the present study were carried out, was purified first by passing through molecular sieve 3A columns, then by twice distillation under 5—10 mmHg (1 mmHg = 133.332 Pa). Methanol and acetonitrile were distilled before use. The other solvents were used without purification of commercially available reagent grade chemicals.

An Al plate and a p-type GaP wafer were used as an anode and a cathode, respectively. The preparation of the GaP cathode, the area of which was *ca.* 0.5 cm^2, was already reported.[8] The electrolytic cell made of quartz was equipped with a water cooled jacket, gas inlet and outlet. The electrode was set in a sealed cell with a silicone rubber stopper which positioned *ca.* 2 cm above the electrolyte. An electrolyte bridge was inserted into the electrolytic cell through the stopper from an air-tight another cell which was filled with the same electrolyte. An electrical connection between the latter cell and an SCE reference was made by using a salt bridge. By placing the one more cell between the electrolytic cell and the reference electrode, probable contamination from the reference electrode was believed to decrease.

All the insertion points of the stopper were sealed with silicone rubber cement to keep the cell assembly air-tight. N_2 was bubbled into the electrolyte after purification with a flow rate of *ca.* 5 ml/min. The purification was done by successively passing N_2 through an alkaline pyrogallol solution, sulfuric acid, water, a column packed with $CaCl_2$ and a column packed with silica gel. Prior to flowing into the electrolyte, the nitrogen gas was pre-saturated with the same solvent as used in the electrolyte. The effluent gas from the cell was passed through a 0.05 mmol dm^{-3} H_2SO_4 trap before exiting to atmospheres. Light from an 1 kW xenon lamp was focused to a diameter of *ca.* 15 mm by using a glass lenz, by which light of wavelengths longer than 350 nm struck on the electrolytic cell. The intensity of the beam was *ca.* 2 W, as determined by a power meter (Coherent Radiation, model 201), and water at room temperatures was flowed through the water-cooled jacket to prevent evaporation of the electrolyte.

Ammonia was analyzed by the method of Kruse and Mellon.[9] Both the electrolyte and the acid trap was analyzed. For this purpose, the electrolyte was protonated with 20 ml of 0.05 mol dm^{-3} H_2SO_4 under air-tight conditions. A known portion of the solution was subjected to distillation in a micro-Kjeldahl apparatus after adding 10 ml of 30% NaOH to the acidified solution. The ammonia in the distillates was collected in 0.05 mol dm^{-3} H_2SO_4, and its amount was determined. The solution in the acid trap was also subjected to the almost same distillation. Hydrazine was determined for the protonated electrolyte solutions. By adding 30% NaOH to the acidified solution, metal salts in the solution precipitated. After the filtration, the hydrazine in the filtrate was determined with *p*-dimethylaminobenzaldehyde.[10]

The current efficiency η for the formation of NH_3 and N_2H_4 was determined by using Eq. 1;

$$\eta = \frac{\text{Moles of } NH_3(N_2H_4) \text{ produced}}{\frac{\text{Coulombs consumed in the electrolysis}}{69480 \times 3\,(4)}}. \quad (1)$$

Results and Discussion

Ammonia Production in Glyme Containing Three Different Redox Agents. In order to investigate whether or not the combination of glyme and titanium tetraisopropoxide is essential as the electrolyte solution to fix N_2 to NH_3, glyme solutions containing $TiCl_3$ and VCl_3 were tested. Current-potential curves of the Al anode and the p-type GaP cathode are shown in Fig. 1, from which it is shown that the onset potential of the anode was negative of that of the illuminated cathode, indicating that photoelectrochemical cells can be constructed. The principal anodic reaction is the dissolution of Al, and the oxidation of the reduced form of the redox electrolyte, which is produced at the illuminated cathode as its main reaction, must be superposed on the dissolution reaction of the anode. The main reaction at the individual electrode is then given by Eqs. 2 and 3;

$$\text{Al anode: } Al = Al^{3+} + 3e^- \quad (2)$$

$$\text{p-type Gap cathode: } 3Ox + 3e^- = 3R \quad (3)$$

where Ox and R represent an oxidant and a reductant of a redox couple, respectively. When the photoelectrochemical cell was operated under short-circuited conditions, the initial photocurrent usually decreased with illumination time, suggesting that the electrode potential of the p-type GaP cathode varied under the short-circuited conditions. In order to eliminate ambiguities introduced by such a nonsteady behavior of photocurrents, experiments were carried out under potentiostatic control.

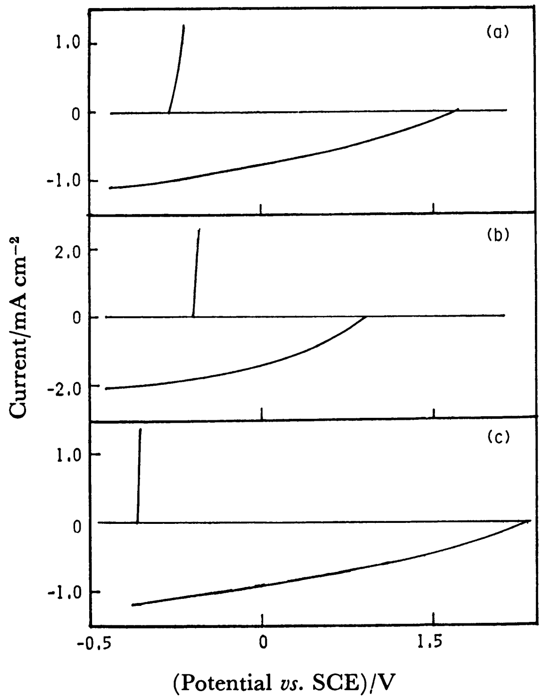

Fig. 1. Current-potential curves for photoelectrochemical cells using an Al anode and a p-type GaP cathode in three kinds of glyme solutions. Electrolyte; (a): 0.5 mol dm^{-3} $Ti[OCH(CH_3)_2]_4$ and 0.75 mol dm^{-3} $AlCl_3$, (b): 0.2 mol dm^{-3} $TiCl_3$ and 0.3 mol dm^{-3} $AlCl_3$, and (c): 0.07 mol dm^{-3} VCl_3 and 0.06 mol dm^{-3} $AlCl_3$.

Table 1 shows results obtained in glyme solutions. In the first row of the table, the results for titanium tetraisopropoxide are given. This electrolyte was already used by Dickson and Nozik.[2] The results for $TiCl_3$ and VCl_3 electrolytes are shown in the second and third rows, from which it is known that ammonia is produced in these electrolytes with a rate almost comparable to that in the titanium tetraisopropoxide electrolyte. Since there is no doubt concerning nitrogen fixation with the electrolyte of glyme–titanium tetraisopropoxide,[2] the glyme–$TiCl_3$ and glyme–VCl_3 electrolytes must also be effective for nitrogen fixation, even though the produced amount was very tiny.

The current efficiency for the formation of ammonia was quite low for all the glyme solutions used. A large fraction of the charge given in the table must have been consumed to reduce the oxidizing agents of the redox couples, *i.e.*, Ti(III) to Ti(II) for $TiCl_3$, V(III) to V(II) for VCI_3, and Ti(IV) to Ti(II) *via* Ti(III) for titanium tetraisopropoxide. If a Pt cathode was used instead of the p-type GaP, no fixation of N_2 was found to occur, as shown in the fourth row of Table 1, suggesting that photosensitization seems to be important for nitrogen fixation.

Nitrogen Fixation Using a Variety of Redox Solutions. In order to catch information on whether or not glyme is essential as the solvent of electrolytes, $TiCl_3$ solutions in different media were tested. As the media, aqueous 0.05 mol dm^{-3} H_2SO_4, methanol and PC were chosen. Results obtained for these electrolytes are shown from the second to fourth rows of Table 2. In the case of the aqueous electrolyte, the hydrogen evolution preferen-

Table 1. Fixation of N_2 at p-type GaP cathode in glyme containing redox agents

Redox species	Its concn / M$^{a)}$	$AlCl_3$ (M)	Onset potential *vs.* SCE / V		Electrolysis potential *vs.* SCE / V	Charge / C	NH_3 produced / mol	Current eff. / %
			Anode	Cathode				
$Ti[OCH(CH_3)_2]_4$	0.5	0.75	−0.27	0.59	−0.2	45.5	0.80	0.51
$TiCl_3$	0.2	0.3	−0.3	0.3	−0.3	62.8	1.98	0.91
VCl_3	0.07	0.06	−0.36	0.8	−0.3	60.4	0.97	0.46
$VCl_3$$^{b)}$	0.07	0.06	−0.8	−0.1	−0.3	60.6	0	0

a) 1 M=1 mol dm^{-3}. b) A Pt cathode was used intead of the p-type GaP.

TABLE 2. FIXATION OF N_2 ON p-TYPE GaP CATHODE IN SEVERAL REDOX SOLUTIONS

Electrolyte				Onset potential *vs.* SCE V		Electrolysis potential *vs.* SCE V	Charge C	Amount fixed µmol		Current eff. %	
Medium (50 ml)	Redox species	Its amount mmol	$AlCl_3$ (mmol)	Anode	Cathode			NH_3	N_2H_4	NH_3	N_2H_4
Glyme	$TiCl_3$	10	15	−0.3	0.3	−0.3	62.8	1.98	u.d.	0.91	u.d.
0.05 M H_2SO_4	$TiCl_3$	25	37.5	−1.0	0	−0.3	71.3	0.0	u.d.	0	u.d.
Methanol	$TiCl_3$	10	15	−1.16	0.24	−0.5	14.9	0.20	u.d.	0.39	u.d.
PC	$TiCl_3$	3	4.5	−0.3	0.4	−0.3	44.5	0.45	0.16	0.29	0.13
PC	VCl_3	5	7.5	−0.25	0.5	−0.2	77.7	0.26	u.d.	0.10	u.d.
PC	$CrCl_3$+ $CrCl_2$	10 1	15	−0.3	0.5	−0.3	26.8	0.24	0.08	0.26	0.12
DMF[a)]	$CrCl_3$+ $CrCl_2$	5 0.5	7.5	−1.0	0.0	−0.5	54.0	0.19	0.0	0.034	0.0
CH_3CN[a)]	VCl_3	*ca.* 8 (saturated)	*ca.* 8	−0.43	0.62	−0.5	7.2	0.14	u.d.	0.19	u.d.

a) Only NH_3 and N_2H_4 trapped in a 0.05 mol dm^{-3} H_2SO_4 trap were determined.

tially took place, as judged from occurring no color change of the electrolyte, resulting in no nitrogen fixation. On the other hand, methanol and PC solutions containing $TiCl_3$ were found to be effective for nitrogen fixation, although the current efficiencies of these electrolytes were very low. In these electrolytes, the color of electrolytes which are characteristics of dissolved Ti(III) were gradually changed in the course of electrolysis. Then, the suggestion was given that the divalent state of the redox agents is necessary for nitrogen fixation to occur. When analyses of hydrazine were made for a $TiCl_3$–PC solution, a positive result for its formation was obtained, as shown in Table 2. It is known from positive results on nitrogen fixation in glyme, methanol and PC solutions that the nature of the solvent does not play a primarily important role in determining whether or not nitrogen fixation takes place.

The results mentioned above give the suggestion that there are a variety of choices for combinations of solvents and electrolytes to fix N_2 in photoelectrochemical processes at p-type GaP cathodes. In order to have experimental evidences for this, additional experiments were performed. Results obtained are summarized from the fifth to eighth rows of Table 2. In the cases of DMF and acetonitrile solutions, it was found that these solvents brought about errors in the determined amounts of NH_3 in the distillates due to contribution of nitrogen originated from the solvent molecules. By this reason, the results for these solutions were obtained only for the acid trap. It is noticed from the obtained results that nitrogen fixation is possible in all the nonaqueous electrolytes tested.

Effects of the Concentration of Electrolyte on Nitrogen Fixation. The current efficiency for the formation of ammonia was investigated as a function of the electrolyte concentration. PC was chosen as the solvent and $TiCl_3$ and $AlCl_3$ as the electrolytes. The molar ratio of $TiCl_3$ to $AlCl_3$ was arbitarily fixed to 2/3. The electrolysis was conducted for 2 d at potentials almost equal to those obtained under short-circuited conditions of the photoelectrochemical cells, which were influenced by the electrolyte concentration as suggested in the captions of Fig. 2. Figure 2 shows the current efficiency for ammonia production (the ordinate in the left hand side) and photocurrents obtained in the initial stage of the electrolysis (the ordinate in the right hand side) as a function of the electrolyte concentration. The magnitude of the cathodic photocurrent in the initial stage of electrolysis was affected by the electrolyte concentration. The current value decreased gradually from those shown in this figure with polarization time probably due to some change in surface conditions of the electrode, as already mentioned. Nevertheless, Fig. 2 gives a strong suggestion that the current efficiency for ammonia production increases with decreasing the cathodic photocurrent.

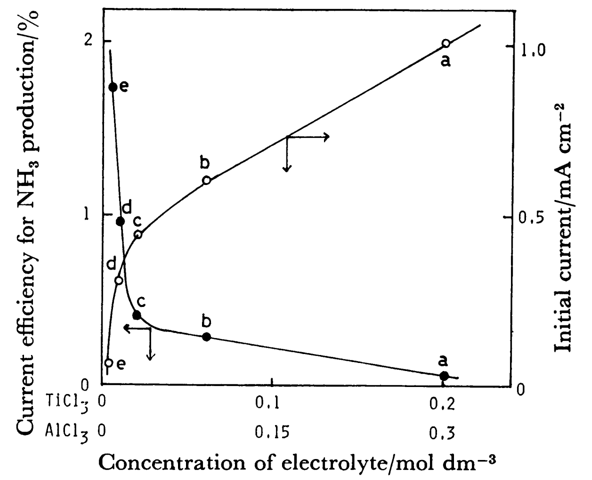

Fig. 2. Effects of the electrolyte concentiation in PC solutions on the current efficiency for NH_3 production and initial photocurrent at the p-type GaP cathode at potentials close to those obtained under short-circuited conditions. The potential (V *vs.* SCE); a: −0.3 V, b: −0.3 V, c: −0.2 V, d: −0.2 V, and e: −0.5 V.

Such a dependency of the current efficiency for ammonia production on the magnitude of cathodic photocurrent will be obtained if either one of the following conditions is fulfilled. (1) N_2 is easily reduced but its solubility is so low that the rate of N_2 reduction is determined by mass transport control of N_2. Since the photocurrent is increased with an increase in the electrolyte concentration due to high reducibility of the redox agents, the current efficiency is decreased with increasing the electrolyte concentration. (2) The concentration of N_2 in the electrolyte is relatively high, but the amount of reducible N_2, which may be bound to the reduced form of the redox agents, is quite low so that the supply of the reducible N_2 to the electrode is limited. In this case, the current efficiency depends on the electrolyte concentration as in the case (1). (3) The rate of the electrochemical reduction of N_2 is quite low and hence almost fixed at a fixed polarization potential regardless of the electrolyte concentration. Since the photocurrent is increased with increasing the electrolyte concentration, the current efficiency decreases in the electrolyte concentration.

No one will believe that the first case is valid. It is well known that nitrogen molecuoes are very stable. Furthermore, it was ascertained that the concentration of dissolved N_2 in the electrolyte was in a range of that usually chosen in kinetic studies of electroactive species. For example, a gas chromatographic analysis of N_2-saturated PC, which was carried out by using a molecular sieve 5A column at 180 °C, showed that the solubility of N_2 is 5.6 mmol dm^{-3}. Such a solubility will be high enough to give an photocurrent of an order of mA cm^{-2} if N_2 were easily reduced, as judged from the reduction of oxygen in aqueous solution which has a comparable solubility, *i.e.*, *ca.* 12 mmol dm^{-3}. As a result, if the case (1) is valid, a much larger current efficiency should be obtained.

As already shown above, V(II), Ti(II), and Cr(II) can assist the reduction of N_2 at illuminated GaP cathodes. This seems to imply that there is some interaction of N_2 with the reduced form of the redox agents. However, the interaction will not be so high as to destroy the N–N bond in a nitrogen molecule, because if the bond breaking would occur, no photosensitization at the GaP cathode would be required for nitrogen fixation. In order to investigate whether or not the case (2) is the most important rate controlling factor, experiments were carried out in electrolytes containing a relatively high amount of the reducing agents. The amount of N_2 bound to the reduced form of the redox agents, if any, must be proportional to the concentration of the reducing agent. If the case (2) is valid, therefore, the current efficiency will be high for an electrolyte rich in the reductant. The experiments were carried out in $AlCl_3$–PC solutions into which either $TiCl_3$ or VCl_3 was dissolved, and the solutions were pre-electrolyzed by using an Al anode and a Pt or an illuminated p-type GaP cathode to prepare Ti(II) or V(II) in the solutions. When the GaP cathode was used, the pre-electrolysis was conducted under Ar atmospheres. By the pre-electrolysis, the electrolytes changed their color, indicating that the reduced form of the redox agents became rich. At this stage, the p-type GaP cathode was polarized under illumination in the prepared electrolytes into which N_2 was continuously bubbled. Results obtained in these experiments are shown in Table 3. According to this table, the current efficiency for production of ammonia was not increased by the pre-electrolysis of the electrolytes, suggesting that the concentration of N_2 bound to the reductant, if any, does not affect significantly on the reduction of N_2. It follows then that the case (3) seems to be most probable as the rate controlling factor for the electrochemical reduction of N_2.

Effects of Water as an Impurity in the Electrolyte on the Production of Ammonia. As a proton source of the ammonia formation, attention was focused to water dissolved in the electrolytes. It was shown by the Karl-Fischer titration method that $TiCl_3$–PC solutions contained 0.29 mg of water for 1 ml of 0.02 mol dm^{-3} $TiCl_3$ and 0.20 mg for the same volume of 0.01 mol dm^{-3} $TiCl_3$. These contents correspond to the water concentration of 0.016 and 0.011 mol dm^{-3}, respectively. If 1 ml of water was intentionally added to 50 ml of the solution, the water concentration increased to 1.1 mol dm^{-3}. According to results obtained by using these aquated PC solutions, the current efficiency was found to be influenced by the water content and was high for solutions of high concentrations, as Table 4 shows. However, it was found that by adding water to PC solutions, the chloride salts in the electrolyte were hydrolyzed, giving rise to precipitates. As a result, the conductivity of solutions decreased. By this reason, more negative potentials were chosen for the electrolysis of the intentionally aquated solutions. Nevertheless, the initial current for the electrolysis was still small compared to that obtained for solutions of no intentional water. As already shown in Fig. 2, the current efficiency for nitrogen fixation was increased by decreasing the current density for electrolysis. Therefore, the enhancement of the current efficiency by introducing water into PC solutions may be ascribable at least in part to the decreasing effect of the current density. Although a simple conclusion may not be drawn from the results given in Table 4, it will be of no doubt that a trace amount of water in the electrolyte can act as a proton source for nitrogen fixation.

TABLE 3. FIXATION OF N_2 IN ELECTROLYTES CONTAINING RELATIVELY HIGH AMOUNT OF REDUCING AGENTS[a)]

Redox species	Its amount mmol	$AlCl_3$ (mmol)	Preelectrolysis[b)] Potential *vs.* SCE V	Preelectrolysis[b)] Charge C	Electrolysis Potential *vs.* SCE V	Electrolysis Charge C	NH_3 (μmol)	Current eff. %
VCl_3	5	7.5	−0.2 (GaP)	19.4	−0.2	4.85	0.12	0.60
$TiCl_3$	1	10	−1.0 (Pt)	172	−0.3	37.8	0.13	0.10
VCl_3	1	5	−0.4 (Pt)	100.5	−0.4	2.36	0.05	0.59

a) The solvent of all the electrolytes was PC. b) The pre-electiolysis was carried out by using an Al anode and a Pt or an illuminated p-type GaP cathode. In the case of the GaP cathode, the pre-electrolysis was conducted under Ar atmospheres.

Table 4. Effects of water on ammonia production at p-type GaP cathode in PC solutions

$TiCl_3$ (M)	$AlCl_3$ (M)	H_2O (M)	Onset potential *vs.* SCE / V		Electrolysis potential *vs.* SCE / V	Initial current / μA cm^{-2}	Charge / C	Amounts of NH_3 produced / μmol	Current eff. / %
			Anode	Cathode					
0.02	0.03	0.016	−0.27	0.45	−0.2	430	17.9	0.24	0.39
0.02	0.03	1.1	−0.8	0.4	−0.5	200	14.3	0.27	0.55
0.01	0.015	0.011	−0.2	0.8	−0.2	300	4.6	0.15	0.94
0.01	0.015	1.1	−0.77	0.3	−0.7	110	3.72	0.19	1.48

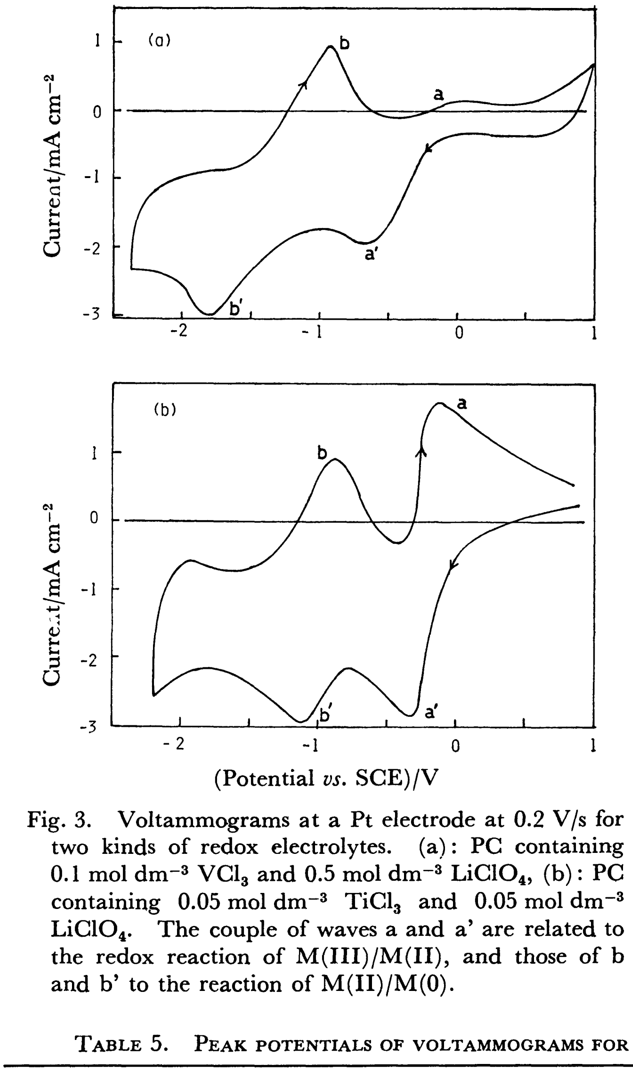

Fig. 3. Voltammograms at a Pt electrode at 0.2 V/s for two kinds of redox electrolytes. (a): PC containing 0.1 mol dm^{-3} VCl_3 and 0.5 mol dm^{-3} $LiClO_4$, (b): PC containing 0.05 mol dm^{-3} $TiCl_3$ and 0.05 mol dm^{-3} $LiClO_4$. The couple of waves a and a' are related to the redox reaction of M(III)/M(II), and those of b and b' to the reaction of M(II)/M(0).

Peak Potentials of Redox Agents. Qualitative information on the reducing power of the redox agents used were compared by measuring peak potentials of voltammograms for the redox reactions at a Pt electrode. The electrolytes used contained not $AlCl_3$ but $LiClO_4$ as an indifferent electrolyte, being different from those used in the experiments of nitrogen fixation. If $AlCl_3$ was used, obtained voltammograms were ill-defined compared to those obtained in $LiClO_4$. By using $LiClO_4$ as the indifferent electrolyte, the obtained results may not directly be applicable to the electrolyte systems used for the experiments of nitrogen fixation, but qualitative information is believed to be still useful.

Two examples of voltammograms are shown in Figs. 3(a) and (b), which were obtained in VCl_3–PC and $TiCl_3$–PC solutions, respectively. The waves a and a' in these figures are connected to the redox reactions between the trivalent and divalent states, b' to the deposition of the metal ions of the divalent state, and b to the re-oxidation of the depositied metal to give dissolution. The voltammograms were also obtained for other electrolytes used in the experiments for nitrogen fixation at 0.2 V/s, and obtained results of peak potentials for individual redox reaction are collected in Table 5.

According to the obtained results, the separation between E_{pc} and E_{pa} is larger than that expected theoretically for a reversible system, which is 0.057 V,[12] suggesting that the value of the peak potentials are varied by the sweep rate chosen for all the electrolytes given in this table. Therefore, rigid comparison of the peak potentials with each other will be of no significance. However, if one assumes that the redox potentials will be obtained as average values of E_{pc} and E_{pa}, it becomes then possible to compare these values with

Table 5. Peak potentials of voltammograms for redox reactions used for nitrogen fixation experiments

Solvent	Redox agent	Its concn / M	(Peak potentials *vs.* SCE)/V[a)] M(III)/M(II)		M(II)/M(0)	
			E_{pc}	E_{pa}	E_{pc}	E_{pa}
Glyme	$Ti[OCH(CH_3)_2]_4$	0.1	−0.65	−0.3	−1.5	−0.93
Glyme	$TiCl_3$	0.1	−0.65	0.05	n.d.[b)]	n.d.
CH_3OH	$TiCl_3$	0.1	−0.5	−0.08	n.d.	n.d.
PC	$TiCl_3$	0.05	−0.3	−0.1	−1.1	−0.8
Glyme	VCl_3	0.1	−0.7	−0.1	−1.45	−1.05
PC	VCl_3	0.1	−0.65	0	−1.8	−0.94
PC	$CrCl_3$	0.02	−0.45	−0.4	−1.4	n.d.

a) The electrolytes contained 0.5 mol dm^{-3} $LiClO_4$ except for glyme–$TiCl_3$ and glyme–VCl_3 where its concentration was 0.3 mol dm^{-3}. Sweep rate: 0.2 V/s. b) Not determined due to no appearence of the peak in the voltammogram. The cathodic current increased monotonically with increasing cathodic polarization in these cases.

one another. By such comparisons, it can be roughly said that the redox potential of Ti(III)/Ti(II) are not greately different among the kind of solvents chosen and that the reducing power of vanadium and chromium ions are also comparable to that of titanium ions. This observation seems to give a basis on the finding that nitrogen fixation occurs with almost the same degree in all the redox electrolytes given in Table 5.

Conclusion. It has been revealed from the present study that nitrogen fixation occurs when the following conditions are fulfilled. (1) Titanium, vanadium and chromium ions are in the divalent state. (2) The electrolytes contain a trace amount of water as an proton source. (3) The cathode can photosensitize the reduction reaction. The fact that the redox agent of a high reducing power is essential for nitrogen fixation seems to suggest that there is some interaction between the redox agent and nitrogen molecules before nitrogen is reduced, as already discussed above. Then the following schemes are evolved as the most probable path for nitrogen fixation.

$$\mathrm{M(III)(solv)}_n \xrightarrow{+e^-} \mathrm{M(II)(solv)}_n \xrightarrow{+N_2} \mathrm{M(II)(solv)}_n\cdots\mathrm{N_2}$$

$$\mathrm{M(II)(solv)}_n\cdots\mathrm{N_2} + 6\mathrm{H_2O} \xrightarrow[\text{photosensitization}]{+6e^-,\ -6OH^-} \mathrm{M(II)(solv)}_n + 2\mathrm{NH_3}$$

where $\mathrm{M(III)(solv)_n}$ and $\mathrm{M(II)(solv)_n}$ represent solvated redox agents having trivalent and divalent states, respectively. The experimental results obtained in the present study were rather scattered, as noticed from comparison of the current efficiency for a variety of redox agents, but the scatters are believed to have been brought about partly by different experimental conditions such as different electrolyte and water concentrations and partly by errors in determination of the amounts of ammonia and hydrazine due to very small amounts of production of these substances. If these are taken into consideration, the results obtained in the present study will be much enough to suggest that there are a variety of choices of electrolyte systems for nitrogen fixation at illuminated p-type GaP cathodes.

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