Electrochemical Generation of Hot Plasma by Pulsed Discharge in an Electrolyte

Kenkichiro Kobayashi,* Yasumasa Tomita, and Masahiro Sanmyo

Department of Materials Science, Faculty of Engineering, Shizuoka University, 3-5-1, Johoku, Hamamatsu, 432-8011 Japan

Received: September 10, 1999; In Final Form: April 6, 2000

Emission is observed at the surface of a Pt working electrode with a small surface area of 1 mm^2 at an applied voltage of 400 V or more, under cathodic polarization, as well as at the voltage of 900 V or more, under anodic polarization. An emission spectrum observed at the cathode in 0.5 M NH_4NO_3 solution consists of H, O, Pt, and H_2 lines which are originated from H_2O and the electrode. The ratio of the intensity of O line at 777.1 nm to H line at 486.1 nm is large at the anode, in comparison with that observed at the cathode. A strong emission from OH radicals is observed in acidic solutions of HNO_3, H_2SO_4, and HCl, and in basic solutions of KOH and NaOH, except for neutral solutions containing NO_3^- ions. The H_2 and Pt emissions are quenched by K^+ ions and are fairly weakened by Na^+ ions. Nevertheless, no quenching of the Pt and H_2 emissions is found in solutions containing Li^+ ions. These results suggest that emission spectra are affected by electrochemical reactions, e.g., gas evolution and electroplating at the electrode surface. Furthermore, it is elucidated that the generation of hot plasma at the cathode is due to not only joule heating of the electrolyte but also the injection of electrons with high kinetic energy of a few hundred electronvolts.

Introduction

Electrochemical generation of hot plasma in an electrolyte has attracted considerable attention from the viewpoints of emission spectrometry and the decomposition of organic compounds responsible for environmental pollution.[1,2] Glow discharge electrolysis (GDE) is well-known as one of methods of electrochemical generation of plasma.[3,4] In GDE, an anode is placed above the surface of an electrolyte, and a high dc voltage is applied between the anode and an electrode immersed in the electrolyte. The electrolyte acts as a cathode, so that the discharge occurs in vapor phase near the surface of the electrolyte. As a particular case of GDE, contact glow-discharge electrolysis (CGDE) has been studied by several authors.[3,5,6] In CGDE, where two electrodes are immersed in an electrolyte, the electrode surface is covered with a thin film of water vapor, and then discharge proceeds inside this thin film. On the other hand, the direct generation of hot plasma in an electrolyte was achieved by pulsed discharge (PD)[7−9] and pulsed diaphragmed discharge (PDD).[10−12] In PDD, a dielectric diaphragm with an aperture is interposed between two electrodes in order to produce a nonuniform electric field in the electrolyte. Plasma is generated by joule heating of the electrolyte near the aperture, so that high input energy is required to initiate the discharge. At an input energy of 1 kJ, in saturated NaCl solution, hot plasma with the electron density of 10^{18} cm^{-3} and the electron temperature of 10^4 K was generated. In this case, emission spectra from the dense plasma consisted of a strong continuum and weak lines of Na. Thus, PDD is not applicable to atomic emission spectrometry. Recently, we found that even at a low input energy of a few joules, strong emission was observed near the cathode with a small surface area of 1 mm,[2] and that emission spectra consisted of many lines and a weak continuum.[1,2] The purpose of the present work is to reveal the mechanism of pulsed discharge in an electrolyte, at low input energy. In order to examine the possibility of the injection of electrons with high kinetic energy, emission measurements were carried out under cathodic or anodic polarization. Emission measurements in several electrolytes were performed for elucidating the effects of electrochemical reactions on emission spectra. The electron temperature and electron density of plasma are estimated from spectroscopic analyses. The correlation of the concentration of Li^+ ions in the electrolyte with the intensity of Li emission is obtained, which can be applied to emission spectrometry. We propose a new mechanism for the generation of hot plasma at the cathode.

Experimental Section

An electrolysis cell was constructed from Pyrex glass. Two Pt electrodes were used as the working and counter electrodes, and no reference electrode was used. The size of the two Pt electrodes was 10 × 50 × 1 mm. The surface of the Pt working electrode was coated with an epoxy resin, except for a small area of 1 mm^2 which was exposed to an electrolyte. Similarly, the surface of the Pt counter electrode was coated in part with an epoxy resin such that a surface area of 50 mm^2 was exposed to the electrolyte. Dc pulses were supplied from a dc power source, a triggered spark gap operating at 400−1200 V, a capacitor of 1 μF, a function generator, and a pulse power source for triggering the spark gap. The frequency of dc pulses was of 5 Hz. The transient emission was detected by a photomultiplier and a digital memory. Emission spectra were measured using a lock-in amplifier and a monochromator with a wavelength resolution of 0. 225 nm, at a slit width of 0.05 mm. Emission measurements were carried out in the range from 350 to 800 nm, at the scan rate of 10 nm/min.

Results

To obtain optimum conditions, e.g., for the concentration of the electrolyte, the surface area of electrodes, and the applied

* Corresponding author. E-mail: kobayasi@mat.eng.shizuoka.ac.jp.

10.1021/jp993218k CCC: $19.00 © 2000 American Chemical Society
Published on Web 06/10/2000

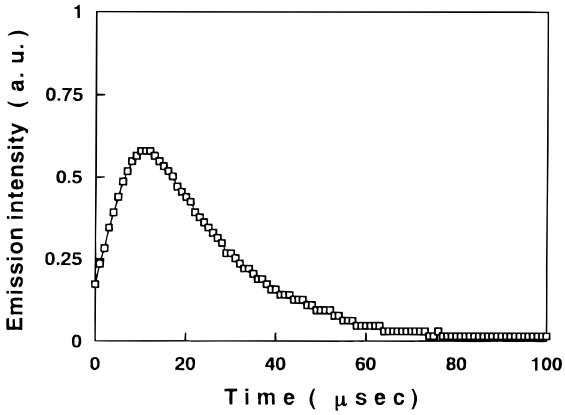

Figure 1. Time dependence of emission at 656.3 nm when dc pulse of 800 V is applied to a Pt cathode, in aqueous 0.5 M NH_4NO_3 solution.

voltage, pulsed discharge was performed in NH_4NO_3 solution which contained no metal ions. Under cathodic polarization, when a negative voltage was applied to the working electrode with a small surface area, emission was observed at the voltage of 400 V or more. The emission was accompanied by the generation of a shock wave. At constant applied voltage, stronger emission and stronger shock wave were observed with a smaller surface area of the working electrode, shorter distance between the working and the counter electrodes, and increasing concentration of the electrolyte. The stronger shock wave expanded the surface area of the working electrode, yielding a decrease of the emission intensity. Taking into account the reliability of emission spectra measurements, we chose 0.5 M electrolyte and the exposed surface area of 1 mm^2.

Figure 1 shows transient emission at 656.3 nm observed at the cathode in 0.5 M NH_4NO_3 solution (at applied voltage of 800 V). As seen in Figure 1, the emission is observed just after a dc pulse has been applied to the electrolysis cell. At any applied voltage, no time lag is seen in the transient emission (not all results are shown). The transient emission has a peak near 10 μs and a duration of about 20 μs. The time at the peak and the duration are dependent on the concentration of the electrolyte and the surface area, but are independent of the applied voltage and wavelength.

At first, we attempted to obtain a spectrum of transient emission as follows: transient emission measurements were carried out at a wavelength increment of 0.5 nm in the range from 800 to 300 nm, and then an emission intensity at time was plotted as a function of wavelength. For weak emissions, however, it was difficult to obtain a transient emission at a high S/N ratio. Alternatively, we employed emission measurements by a lock-in amplifier. For three emissions, i.e., H emissions at 656.3 and 486.1 nm, and O emission at 777.1 nm, their averaged intensities, $I_H(486.1)$, $I_H(656.3)$, and $I_O(777.1)$ were measured by the lock-in amplifier. The ratios of $I_H(486.1)/I_H(656.3)$ and $I_O(777.1)/I_H(656.3)$ were in agreement with those of peak intensities in transient emissions; the averaged intensity was approximately proportional to the intensity of the peak in the transient emission. Therefore, in this paper we present emission spectra recorded by the lock-in amplifier, instead of spectra of the peak intensities in the transient emissions.

Figure 2 shows emission spectra observed at the cathode in 0.5 M NH_4NO_3 solution (at an applied voltage of 600 V). Figure 2a shows the emission spectrum measured using the monochromator alone and Figure 2b the emission spectrum obtained with a short-wavelength cutoff filter set in front of an entrance slit of the monochromator to eliminate light at wavelength <400 nm. The insert in Figure 2 is the transmission spectrum of the Pyrex glass, used for the electrolysis cell. The Pyrex glass is not transparent at wavelength shorter than 300.0 nm. Thus, the emission peaks marked by asterisks in Figure 2a are assigned to the overtone of emissions in the range from 300 to 400 nm. In the emission spectra, there are several lines originating from atomic hydrogen, oxygen, and Pt.[13] For instance, two emission lines at 656.3 and 486.1 nm are assigned to the Balmer series of hydrogen atom, i.e., the transitions from $n = 3$ to $n = 2$ and from $n = 4$ to $n = 2$, where n is the principal quantum number. A strong emission line at 777.1 nm is originated from the transitions of O ($3p\ ^5P \rightarrow 3s\ ^5S^0$). Strong Pt emission lines are seen at 392.3, 367.4, 367.2, 363.9, 362.8, 348.6, 340.9, and 330.1 nm. Besides these emission lines from atoms, there are emission lines arising from H_2 molecules.[14] H, O, and Pt are generated from H_2O and the working electrode. Although a high concentration of NH_4^+ and NO_3^- ions is present in the solution, no emissions from N and NO are present in the emission spectra.

In Figure 3, emission spectra around 656.3 nm in 0.5 M NH_4NO_3 solution are shown as a function of the applied voltage. The peak at 656.3 nm is due to the H emission. As the applied voltage increases, the intensity of the peak is enhanced and, at the same time, the background of the emission spectrum increases significantly. For example, when the applied voltage is changed from 450 to 800 V, the intensity of the emission at 656.3 nm increases by a factor of 3, while the intensity of the continuum at 652 nm increases by a factor of 14. Emission spectra around 486.1 nm are shown in Figure 4. The intensity of the H emission at 486.1 nm is weak compared to that at 656.3 nm, because the population of excited H*, for the quantum number $n = 4$, is less than that of H*, for $n = 3$. The emission spectrum around 486.1 nm is not resolved into a doublet.[15] This is mainly due to the low spectral resolution of the monochromator used in this work. At 750 V or less, the intensity of the continuum around 486.1 nm is fairly low. The lower intensity of the continuum around 486.1 nm is ascribed to the lower temperature of plasma. Figure 5 shows the full width at half-maximum (fwhm) of the emission peaks at 486.1 and 656.3 nm, as a function of the applied voltage. For the emissions at 656.3 and 486.1 nm, the value of fwhm increases monotonically with increasing voltage. Typically, the spectral broadening is caused by collisions, the Doppler effect, and the Stark effect. The spectral broadening for the H emission at 486.1 nm is mainly due to the Stark effect.[15] From these fwhm values, the electron density of the plasma is estimated to be in the range from 4×10^{16} to 4×10^{17} cm^{-3}, at applied voltages of 600 and 800 V.[16] Figure 6 shows the dependence on the applied voltage of the intensity of H_2 emission at 529.1 nm, I_{H_2}, and that of I_H/I_{H_2} ratio, where I_H is the intensity of H emission at 486.1 or 656.3 nm. As the applied voltage increases, the intensity of the H_2 emission increases steeply, whereas the ratio of I_H/I_{H_2} increases slightly. This result indicates that the H emission becomes stronger at a higher voltage, compared to the H_2 emission. At a higher applied voltage, the electron temperature of plasma is raised and thus the dissociation of H_2 into H atoms is expected to proceed more effectively. Hence, the voltage dependence of the I_H/I_{H_2} ratio indicates that the concentration of H_2 is lowered by dissociation, with increasing temperature of the plasma. However, the weak voltage dependence of the I_H/I_{H_2} ratio implies the possibility that hydrogen molecules are generated by another mechanism than the dissociation of H_2O in the hot plasma.

In order to examine the effects of polarization on the emission spectra, a positive voltage was applied to a Pt working electrode

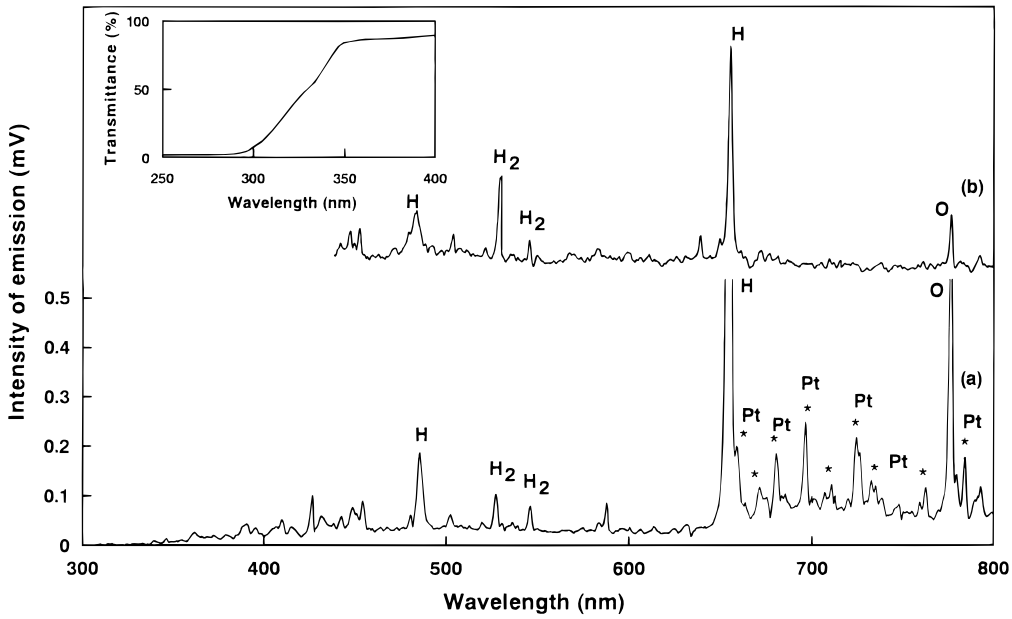

Figure 2. Emission spectra at the cathode, in 0.5 M NH_4NO_3 solution: (a) emission in the range from 350 to 800 nm through Pyrex glass; (b) emission in the range from 430 to 800 nm obtained with a short-wavelength cutoff filter set in front of an entrance slit of the monochromator to eliminate light at wavelength <400 nm. Asterisks in (a) denote overtone of the emission in the range from 300 to 400 nm. The insert shows the transmission spectrum of the Pyrex glass used as the vessel.

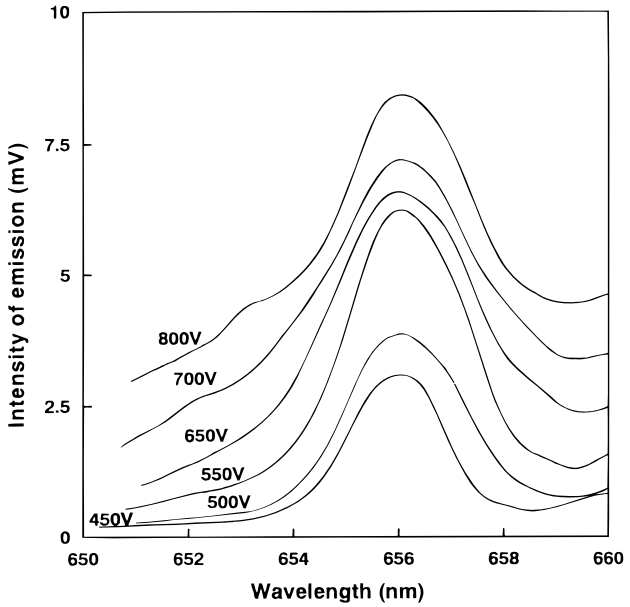

Figure 3. Voltage dependence of emission spectra around 656.3 nm, in 0.5 M NH_4NO_3 solution. The peak at 656.3 nm is due to the H emission.

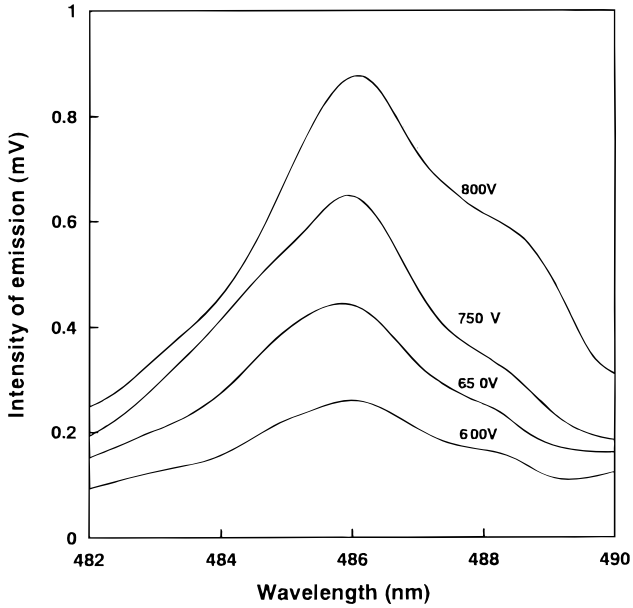

Figure 4. Voltage dependence of emission spectra around 486.1 nm in 0.5 M NH_4NO_3 solution. The peak at 486.1 nm is due to the H emission.

with a surface area of 1 mm^2. One should stress that no emission was observed near the anode up to 850 V, although a shock wave was generated. An appreciable emission was observed at the voltage of 1150 V or more, while the surface of the anode was significantly damaged by the shock wave. Thus, emission spectra, which required a large number of pulses, were recorded at a lower voltage (900 V), while the intensity of emission, at a fixed wavelength, was measured at the voltage of 1150 V or more. An emission spectrum at the anode is shown in Figure 7. Emissions from H and O are detectable, but other emissions cannot be assigned, because of their weak intensity. As seen in Figure 7, the intensity of the H emission recorded, at 656.3 nm, surpasses the O emission, at 777.1 nm. Figure 8 shows a ratio of the intensity of the O emission at 777.1 nm, I_O, to that of the H emission at 486.1 nm, I_H, under anodic or cathodic polarization. The ratio of I_O/I_H decreases with the voltage both under cathodic and anodic polarization. The ratio of I_O/I_H under anodic polarization is slightly higher than that observed under cathodic polarization. This result suggests that the O emission arises to some extent from the O_2 gas evolved at the surface of the anode.

Figure 9 shows emission spectra of several solutions with the same anions: HNO_3, NH_4NO_3, $LiNO_3$, and KNO_3. In the emission spectrum of HNO_3 solution, a new broad peak is observed in the range from 600 to 640 nm, in addition to the emissions from H, O, Pt, and H_2 which are detected in NH_4NO_3 solution. The broad emission disappears when the short wavelength cutoff filter was set in front of the entrance slit of the monochromator in order to eliminate light at wavelength

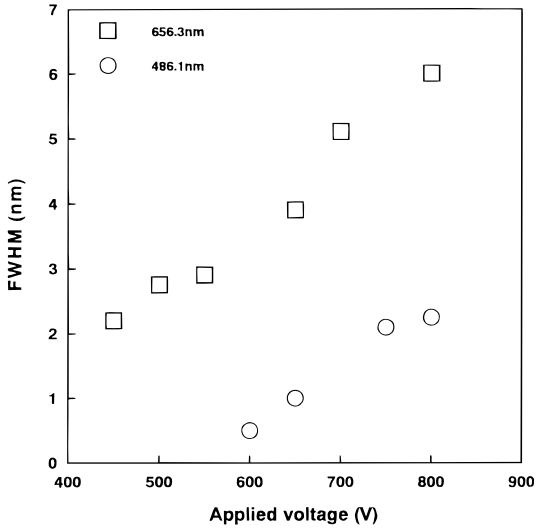

Figure 5. Plots of fwhm of the emission peaks at 486.1 and 656.3 nm, as a function of applied voltage.

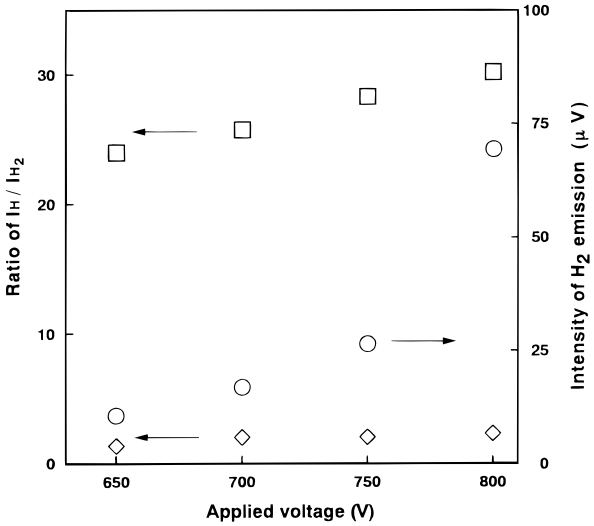

Figure 6. Voltage dependence of the intensity of H_2 emission at 529.1 nm, I_{H_2}, (open circles), and voltage dependence of the intensity ratio of the H emission at 656.3 nm (open squares) or 486.1 nm (open diamonds) to the H_2 emission, I_H/I_{H_2}.

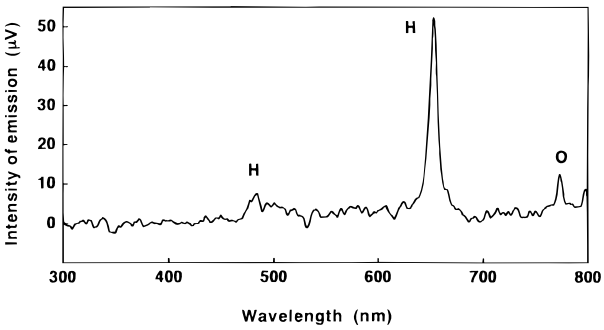

Figure 7. Emission spectrum at a Pt anode in 0.5 M NH_4NO_3 solution; applied voltage is 900 V.

<400 nm. Thus, the broad emission in the range from 600 to 640 nm is the overtone of the emission in the range from 300 to 320 nm. The broad emission is assigned to the band of OH $A^2\Sigma^+ \rightarrow X^2\Pi$. In the emission spectrum of $LiNO_3$ solution, the Li lines are detected at 610.4 and 670.8 nm in addition to the emissions from H, O, Pt, and H_2, but the broad OH emission disappears. An emission spectrum of KNO_3 solution consists

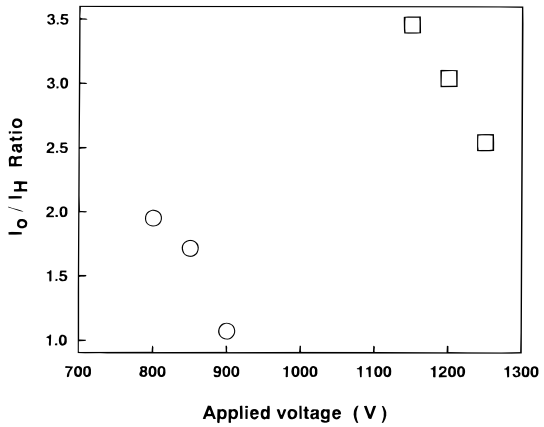

Figure 8. Plots of the I_O/I_H ratio vs applied voltage, under anodic (open squares) or cathodic (open circles) polarization, where I_O is the intensity of O emission at 777.1 nm and I_H is the intensity of the H emission at 486.1 nm.

of H, O, and K lines, but no emissions from Pt, H_2, and OH are seen. In Figure 9, there are two anomalous features of these emission spectra: the OH emission is observed only in HNO_3 solution of low pH value, and the presence of K^+ ions quenches the H_2 and Pt emissions. Emission spectra of HNO_3, H_2SO_4, and HCl solutions of low pH value are shown in Figure 10. In these spectra of all three solutions, the broad OH emission appears, in addition to the emissions from H, O, Pt, and H_2. Although these solutions contain anions, Cl^-, SO_4^{2-}, and NO_3^-, no emissions from Cl, S, and N are seen. Emission spectra of KOH and NaOH solutions of high pH value are shown in Figure 11. K and Na lines are present in these spectra. The broad OH emission is also seen in these spectra of KOH and NaOH solutions. Accordingly, the broad OH emission disappears only in neutral solutions, which contain NO_3^- ions. Another feature in Figure 11 is that the H and Pt emissions disappear in KOH solution, while in NaOH solution they are weakened substantially. Figure 12 shows emission spectra of KCl, NaCl, LiCl, and HCl solutions containing alkali metal ions and H^+ ions. The H_2 and Pt emissions are quenched by K^+ ions and are weakened by Na^+ ions. One striking feature is that Li^+ ions have no influence on the Pt and H_2 emissions, although Li belongs to the alkali metal group.

Figure 13 shows the dependence of the intensity of Li line, at 670.8 nm, on the concentration of Li^+ ions in solutions, which contain (0.5 M NH_4NO_3 + xLiNO$_3$). The highest sensitivity is obtained at 800 V. The detectable minimum concentration of Li^+ ions is of the order of 10^{-5} M, at 800 V. The sensitivity of Li detection is about 10 times lower than that in ICP-AES. A higher sensitivity is not reached by just increasing the applied voltage, because at a higher voltage both the intensity of the Li line and the intensity of the continuum are enhanced. In addition, at a voltage higher than 900 V the damage of the Pt electrode surface by the shock wave becomes important. This damage causes the expansion of the surface area of the Pt electrode, yielding in a decrease of the emission intensity. Thus, the reliability of emission spectra is severely degraded with increasing voltage.

The electron temperature of plasma in a solution containing 0.5 M NH_4NO_3 and 0.002 M $Fe(NO_3)_3$ is estimated from three emission lines of Fe, namely at 381.6, 373.8, and 370.9 nm. In Figure 14, $\log(I\lambda^3/gf)$ is plotted as the excited energy, where λ is the wavelength of emission, g is the degeneracy factor, and f is the transition probability. Values of λ, g, and f for the selected Fe lines are taken from the literature.[17] From the slope

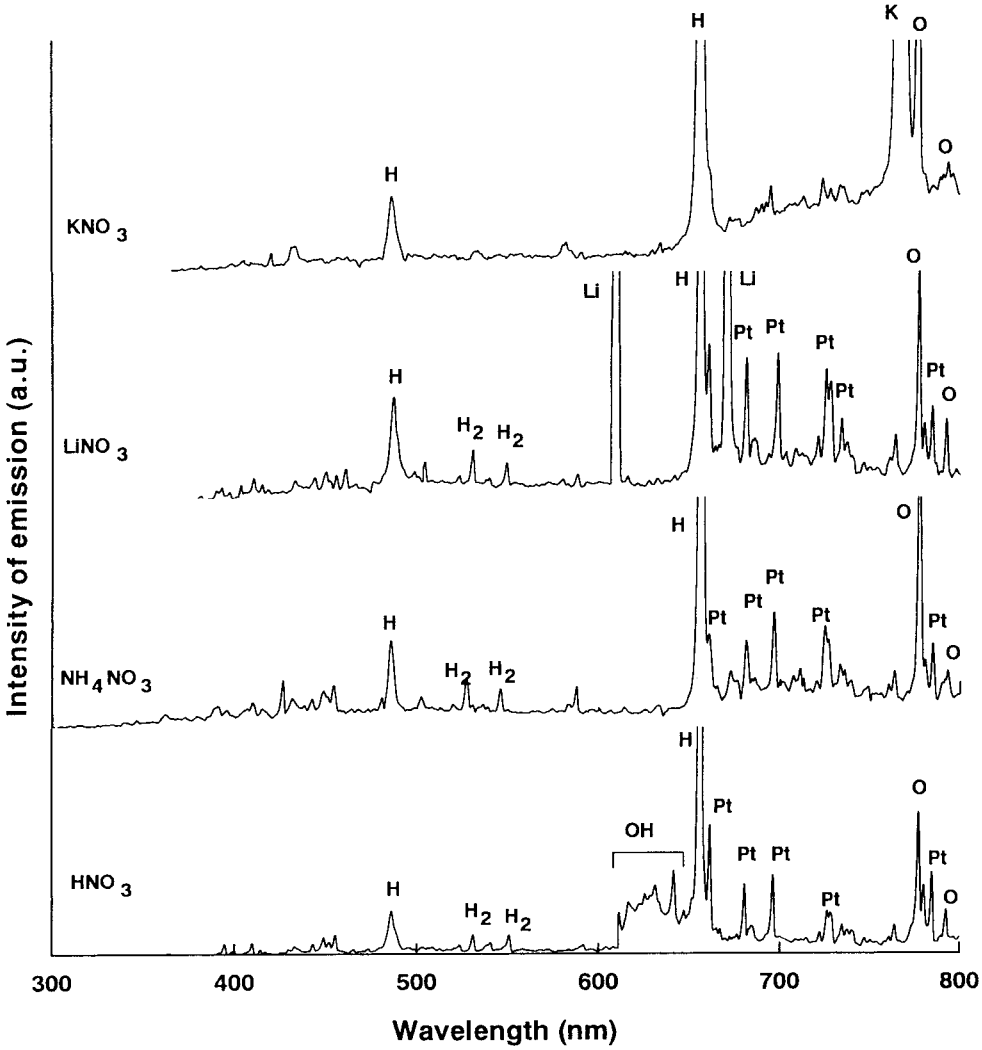

Figure 9. Emission spectra of a series of solutions with common anions: 0.5 M HNO_3, NH_4NO_3, $LiNO_3$, and KNO_3.

of $\log(I\lambda^3/gf)$ vs the excited energy, for the discharges at 600 and 800 V, temperatures of the plasma were estimated to be 13 000 and 15 000 K. The electron temperature of plasma generated by the pulsed discharge increases slightly with increasing voltage.

Discussion

First, we discuss the mechanism of the electrochemical generation of hot plasma in an electrolyte. In PDD, the polarity of the applied voltage has no effect of the initiation of the discharge, as the electrolyte near the aperture of the diaphragm is instantaneously heated to 10^4 K, by passing a large current. In the present work, the polarity of the applied voltage affects significantly the initiation of the discharge. For instance, the emission is observed even at 400 V under cathodic polarization, whereas only a weak emission is observed at voltages above 900 V, under anodic polarization. These results suggest that chemical reactions at the cathode contribute to the initiation of the discharge. One of the electrochemical reactions is the evolution of gas at the electrode surface. For instance, in 0.5 M NH_4NO_3 either hydrogen or oxygen is evolved at the surface of the cathode or anode. Nevertheless, one can rule out the possibility that the discharge is initiated more easily in H_2 gas, compared with that in O_2 gas. The explanation of this phenomenon is that the quenching of the H_2 emission by K^+ ions has no influence on the discharge (see Figures 11 and 12). Next, we discuss the possibility that the discharge is initiated in a thin vapor film covering the electrode surface, as in CGDE. In the pulsed discharge, at fairly large input energy, the electrolyte in contact with the electrode is vaporized and is immediately converted into high-temperature gas phase, i.e., hot plasma. Thus, the film of vaporized solvent is not meaningful in the pulsed discharge, at large input energy. In fact, the formation of a thin vapor film at the electrode surface has not been assessed when observing the hot plasma with a high-speed camera.[18] In the pulsed discharge at low input energy, a thin vapor film may be formed on the electrode surface, if joule heating is insufficient for the generation of hot plasma. In this case, the emission should start when the electrode surface is fully covered with this thin vapor film. As shown in Figure 1, there is, however, no time lag in the transient emission at an any applied voltage. Accordingly, we can exclude the mechanism in which the discharge is initiated in the thin film covering the electrode surface. Another possibility might be that the full coverage of the electrode surface with the thin film is accomplished within 1 μs. To elucidate the contribution of the thin film to the initiation of the discharge, transient measurements within the initial 1 μs are in progress.

In view of the normal glow discharge, electrons are emitted from the cathode into vacuum and emitted electrons bring about the excitation and ionization of atoms in a vacuum.[19] Similarly, electrons with high kinetic energy can be emitted at the interface

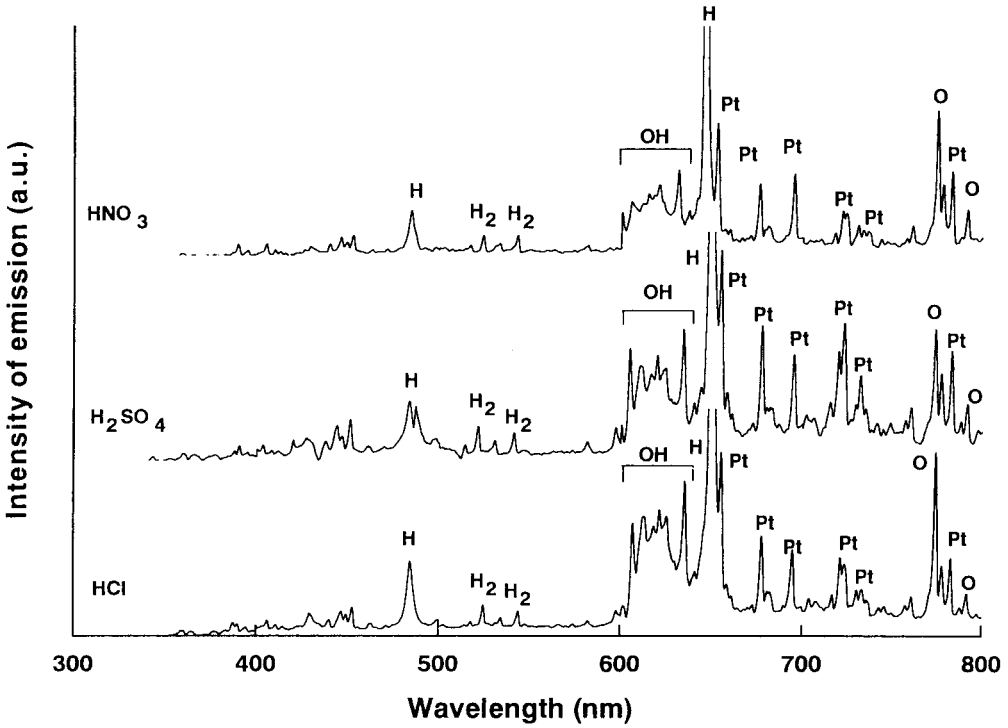

Figure 10. Emission spectra of acidic solutions: 0.5 M HNO_3, H_2SO_4, and HCl.

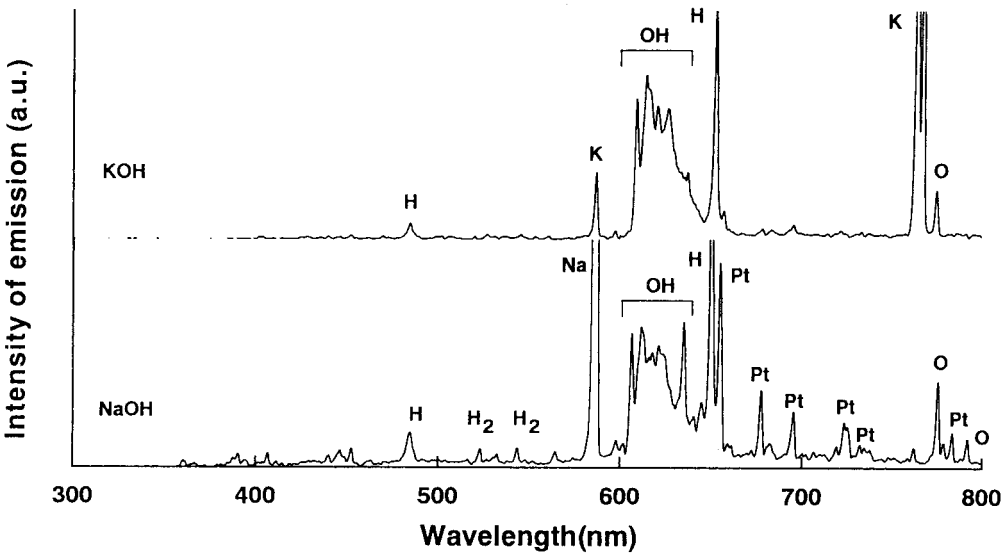

Figure 11. Emission spectra of basic solutions: 0.5 M KOH and NaOH.

of a cathode and an electrolyte in the presence of a high electric field. The emitted electrons can initiate the dissociation of water, excitation of solvent or atoms, the ionization of water, and the neutralization of cations present in the electrolyte.[20,21] Such an electron injection from the cathode is similar to the irradiation of water with an electron beam. Nevertheless, several attempts to find light emission in irradiated water failed, only Cherenkov radiation being detected.[22] For example, Shaeda and Walker[23] examined emission from water irradiated with an intense and short pulse of high-energy electrons, and they concluded that the emission was not originated from electronically excited H_2O, H, and OH molecules. Czapski and Katakis[24] have arrived to a similar conclusion, from studies of light emission in aqueous solutions of T_2O. The reason is that electronically excited energy of H* or O* in the liquid phase is immediately dissipated by the surrounding solvent molecules. On the other hand, strong emissions from H, O, and OH were observed when water vapor was irradiated with a pulsed electron beam.[25,26] Accordingly, in the case of our pulsed discharge in the electrolyte, electronically excited atoms or molecules exist in the gas phase, at high temperature, i.e., in hot plasma. The difference between the electron beam irradiation of water and the electrochemical injection may be attributed to the density of the dissipated energy. The electrochemical injection of electrons takes place at high current density, e.g., charge of 8×10^{-4} coulomb is stored in a capacitor of 1 μF, at an applied voltage of 800 V, and its charge is released within 50 μs; the current density at the 1 mm^2 electrode corresponds to 1.6×10^3 A/cm^2, which is 16 times greater than that in the electron beam irradiation.[22,23] The high-density injection of electrons yields not only the ionization, the excitation, and the dissociation of solvent molecules, but also causes the local heating of the electrolyte by nonradiative decay. Moreover, the electrolyte near the cathode is heated by the flow of a large current. Therefore, at

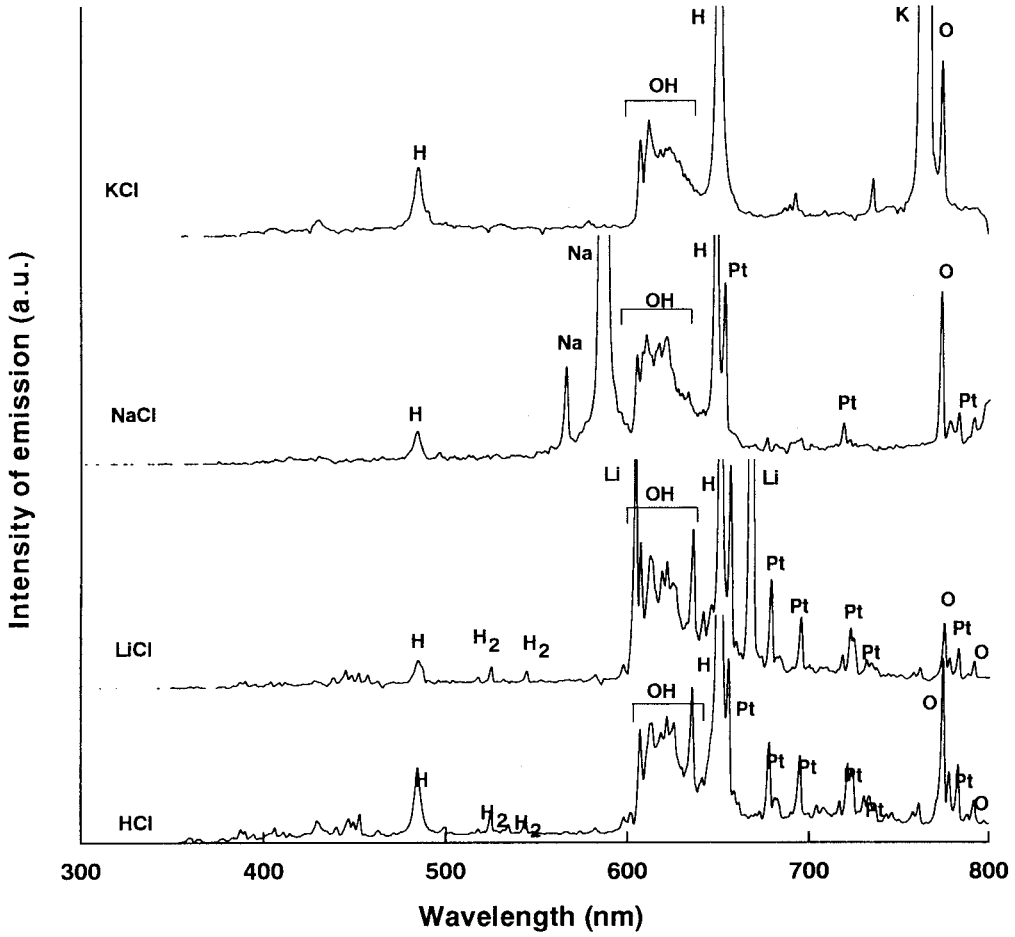

Figure 12. Emission spectra of solutions containing alkali metal ions and H^+ ions: 0.5 M KCl, NaCl, LiCl, and HCl.

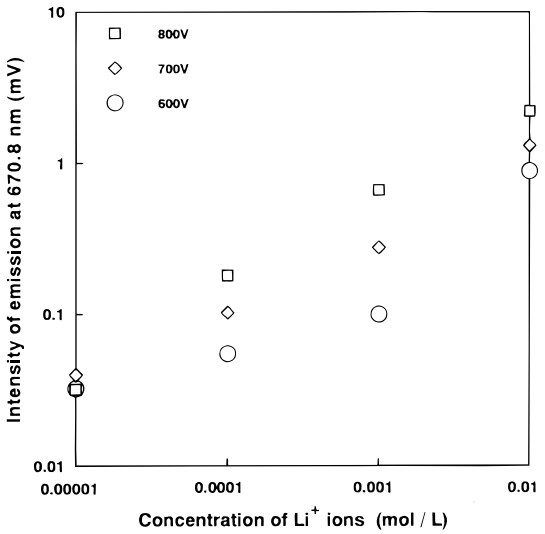

Figure 13. Dependence of the intensity of Li line, at 670.8 nm, on the concentration of Li^+ ions, in solutions of (0.5 M NH_4NO_3 + xLiNO$_3$).

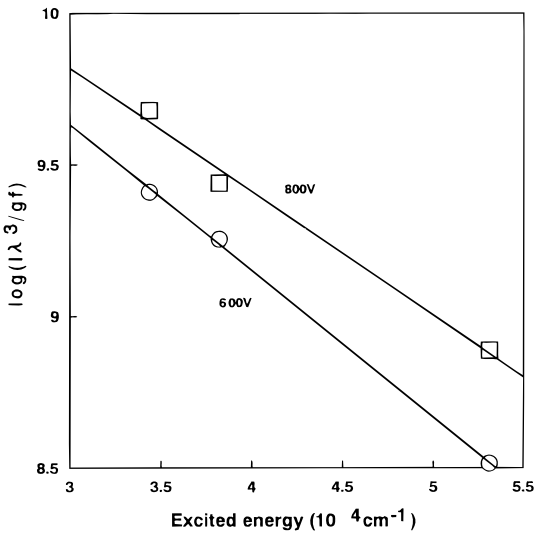

Figure 14. Plots of log($I\lambda^3/gf$) vs excited energy, where λ is the wavelength of emission, g is the degeneracy factor, and f is the transition probability.

the cathode, the electron injection and joule heating contribute to the generation of hot plasma, whereas the hot plasma near the anode is produced only by joule heating, as in PDD.

As discussed in conjunction with Figures 10, 11, and 12, the emission intensity from OH radicals is comparable to the intensity of the H emission. Such a strong OH emission was also found in DD[7] and GDE.[4] According to the calculation of Radovanov and co-workers,[9] in hot plasma at the temperature of 10^4 K, OH concentration is 10^4 times less than that of H atoms. Thus, no large amounts of OH radicals are produced by the decomposition of H_2O in the hot plasma. In our pulsed discharge, the kinetic energy of injected electrons may be of about a few hundred electronvolts, because a part of applied voltage is available for the acceleration of electrons at the interface of the cathode and the electrolyte. The composition of products by the electrochemical electron injection can be estimated from studies on electron beam irradiation of water. For instance, the radiolysis yield (G value) of liquid water with

100 eV electron beam was reported to be $e_{aq}^-(2.5) + OH(2.3) + H(0.6) + H_2(0.45) + H_2O_2(0.85) + H_3O^+(2.5)$.[27] The high yield of OH radicals was a feature of the electron beam irradiation of water. Consequently, the strong OH emission observed by us is consistent with the mechanism in which hot plasma is generated at the cathode in part by the injection of electrons with a few hundred electronvolts.

The experimental finding that the OH emission disappears only in neutral solution containing NO_3^- anions cannot be explained by the composition of hot plasma, in thermodynamic equilibrium. At the plasma temperature of 10^4 K, NO_3^- anions are decomposed into NO molecules having the concentration about 10^3 times less than that of H and O atoms,[9] and the number of NO molecules is independent of the pH value of the electrolyte. The cathodic reduction of NO_3^- in a neutral solution yields NO molecules, whereas NO_2 or N_2O_4 molecules are generated in 0.5 M HNO_3 solution.[28] Only NO molecules can act as scanvagers of OH radicals. Similar quenching of OH radicals was found by adding isopropyl alcohol to the electrolyte.[7] Thus, electrochemical reactions at the cathode affect the emission spectra. The interpretation is consistent with the slight decrease of the I_O/I_H ratio under cathodic polarization (see Figure 8), because hydrogen atoms are produced at the surface of the cathode.

As seen in Figures 11 and 12, the H_2 and Pt emissions are quenched simultaneously by K^+ ions and is weakened by Na^+ ions. Li^+ ions have, however, no influence on either H_2 or Pt emission. This suggests that both H_2 and Pt emissions have the same origin. In other words, the H_2 emission is originated from H_2 molecules adsorbed on the Pt electrode surface. These H_2 molecules are produced mainly by electrochemical reactions, rather than by the dissociation of H_2O in hot plasma. This statement is supported by experimental data that the population of H_2 in hot plasma at 10 000 K is 10^4 times less than that of H atoms.[9] Our finding that the Pt and H_2 emissions are quenched by K^+ ions can be explained by the transient electroplating, as follows: at the early stage of the pulsed discharge, K metal is deposited at the Pt cathode surface by the cathodic reduction of K^+ ions, instead of the generation of H_2. Subsequently, liquid phase water in contact with the cathode surface is converted into hot plasma, by passing a large current. The deposited K metal suppresses the vaporization and excitation of the Pt electrode surface by the hot plasma. After 20 μs, corresponding to the duration of emission, the generation of H_2 by the reaction between the K metal and the liquid phase water can be neglected, because the liquid phase water is converted into hot plasma. In fact, no emission from H_2 has been detected in the emission spectra of solutions that contain K^+ ions. On the other hand, the Pt and H_2 emissions are weakened in the presence of Na^+ ions and are not affected by Li^+ ions. This suggests that few amounts of Li metal are deposited on the Pt cathode surface, and that Na metal and H_2 coexist at the Pt cathode surface. The cathodic reduction may be accelerated on the order of $Li^+ < H^+ \sim Na^+ < K^+$. This interpretation is supported by kinetic studies on the cathodic reduction of alkaline metal ions: the reduction rate constants of Li^+, Na^+, and K^+ ions in aqueous electrolyte at a dropping mercury electrode were reported to be 0.09, 0.18, and 0.7 cm s^{-1},[29,30] The same rate constants were reported for dimethyl sulfoxide to be 3×10^{-4}, 1.4×10^{-2}, and >1 cm s^{-1}.[31]

In the process of the transient electroplating, the emission of K may reflect not only the concentration of K ions in the electrolyte but also that of K metal deposited on the surface of the Pt cathode. By contrast, Li metal deposited on the surface of the cathode may have little contribution to the Li emission; the intensity of the Li emission in Figure 13 is almost entirely due to Li^+ ions contained in the electrolyte. One should emphasize that hot plasma is generated in the solution containing K^+ ions, although the adsorption of H_2 on the Pt electrode is suppressed by the electroplating with K. This means that the evolution of H_2 gas is not a necessary condition for the initiation of the discharge.

In PDD, the discharge was initiated at high input energy, and therefore a dense plasma was generated. For example, at an input energy of 1300 J, the electron density of hot plasma was 10^{19} cm^{-3}, and the pressure of the hot plasma increased up to 300 atm.[11] In this case, emission spectra from the dense plasma consisted of weak lines and a strong continuum. Such a strong continuum is caused by the high electron density and the high pressure of the plasma, because the radiative recombination and the Bremsstrahlung occur more frequently in the dense plasma. On the contrary, in the pulsed discharge at the cathode, the injection of electrons with high kinetic energy lowers the input energy at which the discharge is initiated. Accordingly, one can obtain emission spectra consisting of strong lines and a weak continuum. In the future, the electrochemical generation of hot plasma may be promising for the application in emission spectrometry. Further details on the electrochemically generated plasma emission spectrometry will be discussed in a forthcoming paper.

Conclusion

The polarization of the applied voltage affects significantly the initiation of the discharge; under cathodic polarization, the emission is observed at $\geq$400 V, whereas under anodic polarization, no emission is detected up to 850 V. The intensity of the OH emission recorded in acidic and basic solutions is comparable to the intensity of the H emission. Both the polarization effect and the strong OH emission can be explained by the new mechanism in which electrons with kinetic energy of a few hundred electronvolts are injected from the cathode into the electrolyte. The OH emission disappears only in neutral solutions that contain NO_3^- ions. This quenching is caused by NO molecules, which are generated by the cathodic reduction of NO_3^- ions The disappearance of the Pt and H_2 emissions in the presence of K^+ ions is due to the K metal deposited at the Pt cathode surface. One can concluded from these spectroscopic analyses that the emission spectra at the cathode is affected significantly by the electrochemical reactions prior to the generation of the hot plasma.

References and Notes

(1) Kobayashi, K.; Matsushima, S.; Okada, G. *Proceedings of the 1995 Asian Conference on Electrochemistry*; The Electrochemical Society of Japan: Osaka, Japan, 1995; p 176.

(2) Kobayashi, K.; Sanmyo, M. *Proceedings of ISE, 49th Annual Meeting*; The International Society of Electrochemists: Kitakyushu, Japan, 1998; p 379.

(3) Hickling, A. In *Electrochemical Processing in Glow Discharge at the Gas-Solution Interface*; Bockris, J. O'M., Conway, B. E., Eds.; Plenum: New York, 1971; p 329.

(4) Tezuka, M. *Denki Kagaku* **1993**, *61*, 794.

(5) Sengupta, S. K.; Singh, R.; Srivastrava, A. K. *J. Electrochem. Soc.* **1998**, *145*, 2209.

(6) Azumi, K.; Mizuno, T.; Akimoto, T.; Ohmori, T. *J. Electrochem. Soc.* **1999**, *146*, 3374.

(7) Sato, M.; Ohgigama, T.; Clements, J. S. *IEEE Trans. Ind. Applicat.* **1996**, *32*, 106.

(8) Radovanov, S. B.; Tripkovic, M. R.; Holcclajtner-Antunovic, I. D. *Contrib. Plasma Phys.* **1986**, *26*, 389.

(9) Radovanov, S. B.; Holcclajtner-Antunovic, I. D.; Tripkovic, M. R. *Plasma Chem. Plasma Process.* **1988**, *6*, 457.

(10) Drobyshevskii, É. M.; Dunaaev, Yu. A.; Rozov, S. I. *Sov. Phys. Technol. Phys*, **1973**, *18*, 772.

(11) Drobyshevskii, É. M.; Zhukov, B. G.; Reznikov, B. I.; Rozov, S. I. *Sov. Phys. Technol. Phys*. **1977**, *22*, 148.

(12) Sokolov, V. M. *Sov. Phys. Technol. Phys.* **1984**, *29*, 1112.

(13) Phelps, F. M., III. *MIT Wavelength Tables*; The M.I.T. Press: Cambridge, MA, 1982; Vol. 2.

(14) Pearse, R. W. B.; Gaydon, A. G. *The Identification of Molecular Spectra*; Chapman & Hall: London, 1965.

(15) Pittman, T. L.; Kelleher, D. E. *Proceedings of the Fifth International Conference;* Water de Gruyter: Berlin, 1980*;* p 173.

(16) Griem, H. R. *Plasma Spectroscopy*; McGraw-Hill: New York, 1964.

(17) Jarosz, J.; Mermet, J. M.; Robin, J. P. *Spectrochim. Acta* **1978**, *33B*, 55.

(18) Zhekul, V. G.; Rakovskii, G. B. *Sov. Phys. Technol. Phys.* **1983**, *28*, 4.

(19) Von Engel, A. *Ionized Gases*, 2nd ed.; Clarendon Press: Oxford, UK, 1965.

(20) Ohno, S.; Nagayama, H.; Okazaki, K.; Sato, S. *Bull. Chem. Soc. Jpn*. **1975**, *48*, 2153.

(21) Draganic, I. G.; Draganic, Z. D. *The Radiation Chemistry of Water*; Academic Press: New York, 1971; p 26.

(22) Quickenden, T. I.; Trotman, S. M.; Irvin, J. A.; Sangster, D. F. *J. Chem. Phys*. **1979**, *71*, 497.

(23) Shaede, E. A.; Walker, D. C. *Int. J. Radiat. Phys. Chem*. **1969**, *1*, 307.

(24) Czapski, G.; Katakis, D. *J. Phys. Chem.* **1966**, *70*, 637.

(25) Quickenden, T. I.; Irvin, J. A.; Sangster, D. F. *J. Chem. Phys*. **1978**, *69*, 4395.

(26) Freeman, C. G.; Quickenden, T. I.; Sangster, D. F. *J. Chem. Phys*. **1984**, *80*, 2336.

(27) Walker, D. C. *Q. Rev. Chem. Soc*. **1967**, *21*, 79.

(28) Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solution*; Pergamon Press: New York, 1966.

(29) Sluyters-Rehbach, M.; Sluyters, J. H. *Electrochim. Acta* **1966**, *11*, 73.

(30) Imai, H.; Delahay, P. *J. Phys. Chem*. **1962**, *66*, 1683.

(31) Hills, G. J.; Peter, L. M. *J. Electroanal. Chem.* **1974**, *50*, 175.