Hydrogen Pair-Ion Production by Catalytic Ionization

Wataru OOHARA and Osamu FUKUMASA[1)]

Department of Electronic Device Engineering, Yamaguchi University, Ube 755-8611, Japan
[1)]*Ube National College of Technology, Ube 755-8555, Japan*

(Received 7 December 2009 / Accepted 17 February 2010)

To develop a hydrogen pair-ion plasma source comprising only hydrogen atomic pair ions, i.e., H^+ and H^- ions, the efficient production of pair ions is required. When discharged hydrogen plasma is used to irradiate a Ni catalyst, pair ions are produced on the catalyst surface. Hydrogen chemisorption on the catalyst and the electronegativity of the catalyst material are found to affect pair-ion production.

Keywords: hydrogen pair ion, plasma irradiation, porous catalyst

DOI: 10.1585/pfr.5.S2106

1. Introduction

Pair plasmas comprising only positively and negatively charged particles of equal mass have garnered attention because they maintain space-time symmetry [1, 2]. Instead of the electron-positron pair plasmas studied in high-energy physics and astrophysics [3, 4], a fullerene pair-ion plasma, consisting of positive and negative ions of equal mass (C_{60}^+ and C_{60}^-), has been generated, and its collective phenomena have been investigated experimentally [5–8]. The response frequency of the pair-ion plasma is limited to narrow bandwidths below 50 kHz because the ions are massive. To extensively investigate the physical properties of pair plasmas, particularly their wave-propagation characteristics at higher frequencies, a hydrogen pair-ion plasma source is being developed, because hydrogen atomic pair ions, i.e., H^+ and H^- ions, are the lightest ions and have high response frequencies to electromagnetic fields. Several difficulties must be overcome to develop this plasma source. The pivotal problem is the efficient production of H^- ions. The research and development of negative-ion sources have been extensively performed for more than 20 years in connection with neutral beam injection (NBI) heating for fusion-oriented plasmas [9, 10] and ion guns for proton accelerators [11]. The production methods of H^- ions [12] are classified into volume production [13, 14] and surface production due to contact ionization.

The electronic work function on the surface of electrodes used for H^- extraction is described by applying a thin cesium coating. The surface electrons of the electrodes transfer easily to hydrogen atoms approaching the surface, improving the production efficiency of H^- ions. However, cesium, which has a low evaporation temperature, is easily vaporized and ionized, and Cs^+ ions mix in the plasma; thus, cesium cannot be used here to generate hydrogen pair-ion plasma. The mechanism of the volume-production method has been investigated; H^- ions are known to be produced by the dissociative attachment of slow plasma electrons to highly vibrationally excited hydrogen molecules, which are produced mainly by the collisional excitation of fast electrons. Two regions with high and low electron temperatures are required for H^- production. The generation of a pair-ion plasma requires the production of equal quantities of H^+ and H^- ions and the absence of impurities such as electrons and other ions [15]. It is difficult to satisfy these conditions if contact ionization or volume production is adopted. In this study, an atomic ion production process is considered in which atomic hydrogen is produced in the first stage, and ionized in the second stage. Metals that undergo a dissociative adsorption reaction with hydrogen are located in groups 4-6 and 8-10 of the periodic table and have been minutely investigated in the field of catalytic chemistry. Nickel (Ni), which is easily workable, is chosen as a base material, and the relationship between the surface reaction and pair-ion production is investigated.

2. Experimental Apparatus

To generate the hydrogen pair-ion plasma, a hydrogen discharge plasma is generated under a uniform magnetic field of 65 mT. H^- ions are not produced by volume production in the discharge region because of the presence of fast electrons. A schematic diagram of the experimental setup is shown in Fig. 1. The apparatus for generating the plasma comprises mainly a Penning ionization gauge (PIG) discharge component and a plasma irradiation component. Two tantalum cathodes are located on opposite sides of a water-cooled grounded cylinder with an inner diameter of 7.5 cm and length 15 cm. A 0.5-mm-diameter tungsten filament, biased at the same voltage as the cathodes, is set in front of one of the cathodes to supply thermionic electrons. Electrons are accelerated in a sheath formed in front of this cathode and injected into the

author's e-mail: oohara@yamaguchi-u.ac.jp

space between the two cathodes; most of the electrons are reflected in a sheath in front of the opposite cathode (anticathode) because the same voltage V_k is applied to both cathodes. Since the electrons are electrostatically confined between the two cathodes along the magnetic field lines, neutral particles can be efficiently ionized by electron impact, producing H^+, H_2^+, and H_3^+ ions in this region. An additional cylindrical anode is set concentrically with the water-cooled cylinder, which can be positively biased at V_a relative to the cathode voltage V_k. Electrons pass transversely across the magnetic field lines as a result of their collisions and reach the additional cylindrical anode; thus, the discharge current is equal to the anode current I_a. The central part of the anticathode plate is a tungsten grid of 50 mesh with a diameter of 3 cm through which the discharged hydrogen plasma can pass. A commercially available porous Ni plate (Celmet, Sumitomo Electric Toyama Co., Ltd.) is set at the exit of the plasma source, which acts a catalyst with a porous body of 47-53 cells/inch, a pore size of 0.55 mm, a thickness of 5 mm, a specific surface area of 2,800 m^2/m^3, and a porosity of 95%. The porous catalyst can also be heated by a sheath heater. The temperature at the side of the porous plate is measured by a thermocouple. The porous catalyst is grounded, and the electric field between the porous plate and the anticathode is determined by V_k. The kinetic energy of the positive ions irradiated to the porous catalyst can also be controlled by V_k. In normal operation, the plasma is generated at a fixed voltage of $V_a \sim +160$ V, and the irradiation energy of the positive ions is about 120 eV at $V_k = 0$ V and lower when $V_k < 0$ V. However, electrons are also accelerated when $V_k < 0$ V; ionization occurs in front of the porous catalyst, the irradiation flux increases, and both the irradiation energy and the flux change. Therefore, V_k is fixed at 0 V, and the irradiation energy is almost unchanged here. The irradiation flux and the porous plate temperature are examined in relation to the quantity of pair ions produced. The back-pressure of the vacuum system is 1×10^{-4} Pa. During operation, a continuous flow of hydrogen is maintained at 70 sccm, and the operating pressure in the source is about 4×10^{-2} Pa. The downstream plasma parameters are measured using a Langmuir probe at $z = 22$ cm, where the source exit is located at $z = 0$ cm.

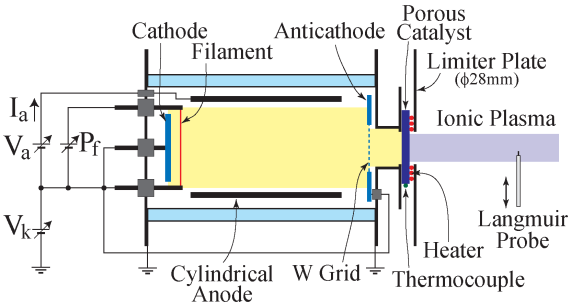

Fig. 1 Schematic diagram of experimental setup for generating penetration-type plasma. Hydrogen plasma generated by PIG discharge is used to irradiate porous catalysts with additional heating.

3. Results and Discussion

PIG-discharged plasma is used to irradiate the Ni porous catalyst; all electrons and positive ions are terminated at the catalyst surface. The dependence of the production of pair ions on the porous plate temperature and irradiation flux is shown in Fig. 2 (a) for a pure Ni porous catalyst, where the irradiation flux increases proportionally with I_a. Without additional heating, the porous plate temperature is determined by the plasma irradiation, and the temperature of the pure Ni porous plate is 277°C at $I_a = 2$ A. An ionic plasma is observed at $z > 0$ cm. The positive- and negative-saturation currents of the probe, I_+ and I_-, are obtained at probe bias voltages of $V_p = -200$ V and +200 V, respectively. Since electrons detached from H^- ions by collisions with neutral H_2 can be neglected for low plasma density and low-energy H^- ions [15], I_- appears to be the only negative-ion current. The current ratio

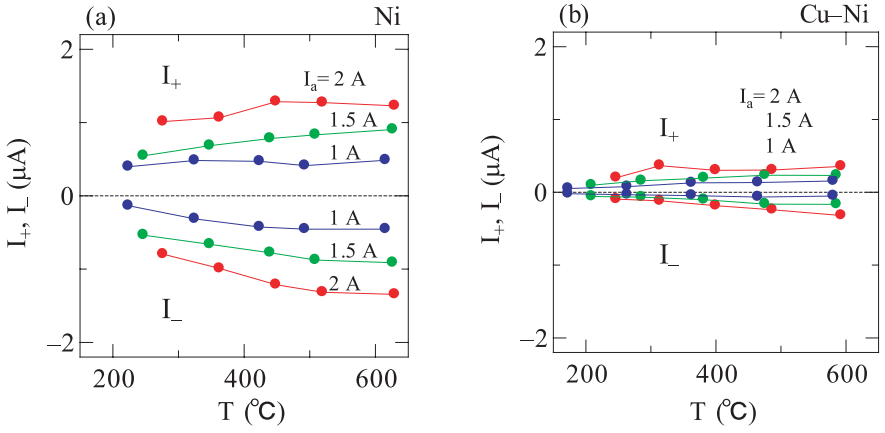

Fig. 2 Dependence of I_+ and I_- on porous plate temperature T and discharge current I_a. Irradiation flux increases proportionally with I_a. Porous catalysts of (a) pure Ni and (b) Cu-Ni alloy are used to vary the amount of hydrogen chemisorption.

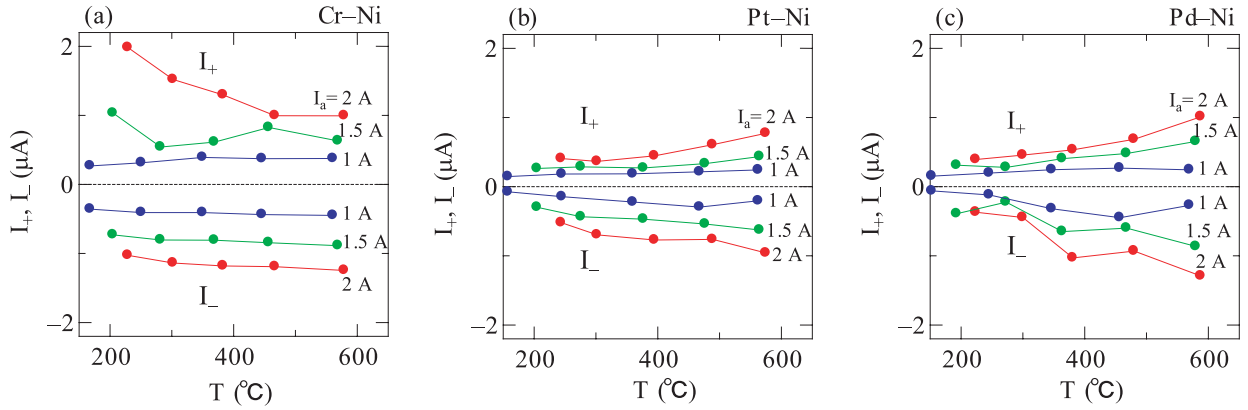

Fig. 3 Dependence of I_+ and I_- on catalyst temperature T and discharge current I_a. Irradiation flux increases proportionally with I_a. Porous catalysts of (a) Cr-Ni, (b) Pt-Ni, and (c) Pd-Ni alloys are used to vary the electronegativity.

I_-/I_+ is close to 1, indicating an ionic plasma comprising only positive and negative ions without electrons. $I_\pm$ both increase proportionally with I_a; that is, the number of pair ions produced increases proportionally with the irradiation flux. The production of H^- ions is particularly affected by the irradiation flux and the porous plate temperature, but the production of H^+ ions appears to be restricted to maintain quasi-neutrality. Thus, the ready production of H^+ ions is attributable to the catalyst material.

Hydrogen atoms are produced by dissociative adsorption on the catalyst surface, and the relationship between hydrogen chemisorption and ion production is considered. We focus on the chemical nature of the catalyst, in particular the position of the elements comprising the catalyst in the periodic table. Ni is located in group 10, and copper (Cu) is located in group 11. Ni is a good catalyst for the dissociative adsorption of hydrogen, similar to platinum, but Cu, a homolog of gold, is a poor catalyst. For Ni, Cu, and their alloys, the chemisorption of hydrogen has been measured [16]. The quotient α of the number of hydrogen atoms chemisorbed divided by the number of xenon atoms physisorbed is an appropriate parameter for characterizing hydrogen chemisorption per unit surface area. The value of α for pure Ni is $\alpha_{Ni} \sim 3.9$, and that for pure Cu is $\alpha_{Cu} \sim 0$. The ratio of the values for Cu-Ni alloys to that for Ni is constant, $\alpha_{alloy}/\alpha_{Ni} \sim 0.23$, for atomic fractions of Cu of 2-80% with a constant surface composition. A thin Cu film is formed on the surface of a pure Ni porous plate through galvanic electroplating. The plate is heated to about 600°C in vacuum, and a Cu-Ni alloy porous plate of 25% Cu and 75% Ni is fabricated. Impurities on the surface are removed by hydrogen reduction due to irradiation. The dependence of the production of pair ions on the porous plate temperature and irradiation flux is shown in Fig. 2 (b) for a Cu-Ni alloy porous catalyst.

Without additional heating, the temperature of the Cu-Ni alloy porous plate is 247°C at I_a = 2 A, which differs from that of the pure Ni porous plate, although the irradiation conditions are the same. The porous plate temperature is thus controlled only by the additional heating. $I_\pm$ both increase proportionally with I_a. $I_\pm$ are lower for the alloy porous catalyst than for the pure Ni porous catalyst. The value of $I_{\pm alloy}/I_{\pm Ni}$ (≈ 0.3) is close to that of $\alpha_{alloy}/\alpha_{Ni}$ (≈ 0.23), although the catalyst plate temperature and the shape of the catalyst differ. Thus, we can conclude that pair-ion production is related to the chemisorption of hydrogen atoms. An increase in the porous plate temperature affects ion production but has less effect than an increase in the irradiation flux.

Next, we examine the effect of electronegativity, which describes the ability of an atom to attract electrons toward itself, on the production of H^- ions. The electronegativity of Ni is 1.8 (that of hydrogen is 2.2) in Pauling units, and we vary the electronegativity by changing the catalyst material. Like Ni, platinum (Pt) and palladium (Pd) are located in group 10, and their electronegativities are both 2.2, which is higher than that of Ni. On the other hand, the electronegativity of chrome (Cr), located in group 6, is 1.6, which is lower than that of Ni. Cr, Pt, and Pd are good catalysts for the dissociative adsorption of hydrogen. Thin films of Cr, Pt, and Pd are formed on the surface of a pure Ni porous plate by galvanic electroplating. The coated plates are heated to about 600°C in vacuum, and Cr-Ni, Pt-Ni, and Pd-Ni alloy porous plates are fabricated by the same procedure as that used for the Cu-Ni alloy porous plate. The dependence of the production of pair ions on the porous plate temperature and irradiation flux is shown in Figs. 3 (a), (b), and (c) for Cr-Ni, Pt-Ni, and Pd-Ni alloy porous catalysts, respectively.

$I_\pm$ tend to increase proportionally with I_a and T, except for the Cr-Ni alloy porous catalyst at I_a = 1.5 and 2 A, at which the irradiation flux increases proportionally with I_a. $I_\pm$ are lower overall for the Pt-Ni and Pd-Ni alloy porous catalysts than for the pure Ni porous catalyst. On the other hand, for the Cr-Ni catalyst, $I_\pm$ are almost the same or more, and pair ions are efficiently produced at a low temperature (< 400°C). These results show that the electronegativity of the catalyst material af-

fects the production of hydrogen pair ions. The work functions of Ni (5.15 eV), Cu (4.65 eV), Cr (4.5 eV), Pt (5.65 eV), and Pd (5.12 eV) [17] are relatively high and the contact-ionization probability of H^- ions is infinitely close to zero. The catalytic activity for hydrogen is important here, whereas the work function does not affect the ionization.

4. Conclusion

To generate a hydrogen pair-ion plasma, porous catalysts of Ni and several Ni alloys are used to produce hydrogen atomic pair ions, i.e., H^+ and H^- ions. When hydrogen plasma generated by PIG discharge is irradiated to porous catalysts of pure Ni and Cu-Ni, Cr-Ni, Pt-Ni, and Pd-Ni alloys along the magnetic field lines, pair ions are produced from the back side of the irradiation plane. Increases in the irradiation flux and porous plate temperature affect the number of pair ions produced. The production properties of H^+ and H^- ions are different; H^+ ions are more easily produced than H^- ions using a pure Ni catalyst. To change the hydrogen chemisorption and the electronegativity of the catalyst material, Cu-Ni, Cr-Ni, Pt-Ni, and Pd-Ni alloy porous catalysts are fabricated and plasma irradiation is performed as with the pure Ni porous catalyst. Pair-ion production appears to be related to the number of hydrogen atoms chemisorbed and the electronegativity of the catalyst material.

Acknowledgements

The authors thank Dr. K. Tsumori and Dr. Y. Takeiri for their collaboration and Dr. R. Hatakeyama for his encouragement. This work was supported by NIFS (NIFS09KKMB004) and a Grant-in-Aid for Young Scientists (A) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

[1] N. Iwamoto, Phys. Rev. E **47**, 604 (1993).
[2] G. P. Zank and R. G. Greaves, Phys. Rev. E **51**, 6079 (1995).
[3] M. D. Tinkle, R. G. Greaves and C. M. Surko, Phys. Plasmas **2**, 2880 (1995).
[4] H. Boehmer, M. Adams and N. Rynn, Phys. Plasmas **2**, 4369 (1995).
[5] W. Oohara and R. Hatakeyama, Phys. Rev. Lett. **91**, 205005 (2003).
[6] W. Oohara, D. Date and R. Hatakeyama, Phys. Rev. Lett. **95**, 175003 (2005).
[7] W. Oohara and R. Hatakeyama, Phys. Plasmas **14**, 055704 (2007).
[8] W. Oohara, Y. Kuwabara and R. Hatakeyama, Phys. Rev. E **75**, 056403 (2007).
[9] M. Kuriyama *et al.*, Fusion Eng. Des. **39**-**40**, 115 (1998).
[10] Y. Takeiri *et. al.*, Rev. Sci. Instrum. **70**, 4260 (1999).
[11] H. Oguri, T. Tomisawa, M. Kinsho, Y. Okamura and M. Mizumoto, Rev. Sci. Instrum. **71**, 975 (2000).
[12] M. Bacal, Nucl. Fusion **46**, S250 (2006).
[13] O. Fukumasa, J. Phys. D **22**, 1668 (1989).
[14] O. Fukumasa and S. Mori, Nucl. Fusion **46**, S287 (2006).
[15] W. Oohara and O. Fukumasa, J. Plasma Fusion Res. SERIES **8**, 860 (2009).
[16] W. M. H. Sachtler and P. Van Der Plank, Surf. Sci. **18**, 62 (1969).
[17] H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).