

Metal ion Sorption on Activated Carbons in Dilute Aqueous Solutions

Jae Sik Hwang, Yongju Jung, Jei-Won Yeon, Kwang Yong Jee

^a Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Dukjin-dong, Yuseong-gu, Daejeon 305-701, Korea

1. Introduction

Recently, many kinds of carbon materials including nanostructured carbons and carbon blacks with a high surface area have been studied as a sorption material or a metal catalyst support for an application to electrocatalysts of the electrochemical reaction in fuel cells [1-4]. To prepare carbon-supported Pt or Pt-based alloy catalysts, various techniques including the impregnation method, the microemulsion method, the colloidal method, and the electrodeposition method have been suggested [1-4].

Here we examine metal ion sorption on activated carbons in dilute aqueous solutions and evaluated selectivity property of the sorbent in mixture solutions.

2. Experimental

A microporous activated carbon (F400, Calgon Carbon Corporation, USA) was used as a sorbent. The F400 is a microporous carbon which has a specific surface area of about 1000 m²/g and a micropore volume of 0.326 cm³/g. To enhance the sorption property, the surface of the F400 was modified with PEI and CMPEI by agitating a mixture solution of the F400 and PEI in an aqueous solution at pH 5 for 6 hr. The PEI (MW = 750,000) and CMPEI (MW = 50,000) were obtained from BASF and used as received. We examined the effect of a PEI coating on the dispersion of F400 by performing adsorption tests of Pt(IV) on the F400 in dilute aqueous solutions of 20 ppm Pt(IV) at pH = 4.0. The equilibrium adsorption tests of Pt(IV) on a F400, a PEI-coated F400 with a 2.5 wt% PEI content and a nano-sized Super P carbon black (TIMCAL) were performed under a constant ionic strength of 0.1 M NaNO₃ at pH = 2.5. The Super P carbon black has a particle size of ca. 40 nm and a specific surface area of ca. 62 m²/g. In this work, PtCl₄ (Aldrich Chemical Co., Inc.) was used as a Pt precursor. The amount of Pt(IV) adsorbed onto the adsorbents at an equilibrium was calculated by measuring the final Pt(IV) concentration in the adsorption medium by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Horiba Ultima 2). Furthermore, sorption selectivity of the activated carbons was evaluated in various mixture solutions.

3. Results and Discussion

3.1 Dispersion of Activated Carbon

The effect of PEI on the dispersion of the F400 was examined by measuring the adsorption amount of Pt(IV) on the F400 in a dilute aqueous solution of 20 ppm Pt(IV) at pH = 4.0. It was observed that the amount of Pt(IV) adsorbed was greatly increased when the surface of the F400 was coated with PEI as shown in Fig. 1. Especially, the F400 showed an increase in the adsorption amount of Pt(IV) by ca. 7% when it was coated with a 2.5 wt% PEI. So, we carried out equilibrium adsorption tests on the PEI-coated F400 with a 2.5 wt% PEI content, which is denoted as PEI(2.5)/F400.

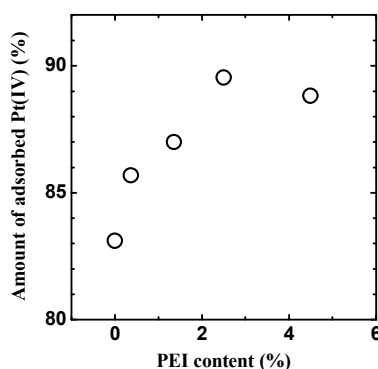


Figure 1. Effect of a PEI coating on the adsorption of Pt(IV) on the F400 at 22°C.

3.2 Adsorption Isotherms

Fig. 2 shows the adsorption isotherm of Pt(IV) on the Super P, the F400 and the PEI(2.5)/F400 at pH 2.5. It was observed that the F400 showed at least a three times larger adsorption capacity of Pt(IV) than the Super P. We think that this may be caused by the large surface area of the F400 on which Pt(IV) can be adsorbed. We can clearly see that the PEI(2.5)/F400 which has relatively high dispersion characteristics in an aqueous solution clearly showed an increased adsorption capacity of Pt(IV), compared to the pure F400 (Fig. 2).

In the case that an adsorbent has poor dispersion characteristics in an adsorption media, it is generally not easy to get accurate thermodynamic data concerning its adsorption phenomena. So, we extracted some useful information from the adsorption data of Pt(IV) on the PEI-coated F400. The adsorption isotherm of Pt(IV) on the PEI(2.5)/F400 was analyzed using various isotherm models including the Langmuir adsorption isotherm model [5]. The Langmuir isotherm shows excellent fit to the experimental adsorption data, thus providing the extremely high correlation coefficients ($R^2 = 0.9962$).

This strongly supports that the adsorption of Pt(IV) onto the PEI-coated F400 follows the Langmuir model. The Q_0 and K_L , which were calculated from the slope and intercept of the regression line, were 435 mg/g and 3.45×10^{-2} L/mg, respectively. The small value of the constant K_L indicates that the heat of the adsorption is low.

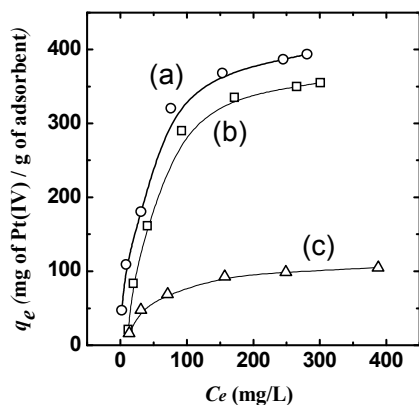


Figure 2. Adsorption isotherm of Pt(IV) on the PEI(2.5)/F400 (a), the F400 (b) and the Super P (c) at pH = 2.5.

3.2 Sorption Selectivity

Fig. 3 shows the sorption selectivity of activated carbons (F400) modified with CMEPI in a ternary solution containing Cu(II), Co(II) and Ni(II). The modified F400 showed the best adsorption selectivity for Cu(II).

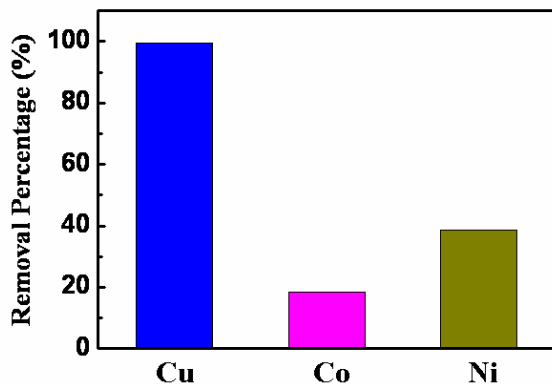


Figure 3. Sorption selectivity of F400 in a ternary solution of Cu(II), Co(II) and Ni(II): initial concentration of metal ions = 5 ppm.

3. Conclusion

We examined metal ion sorption on activated carbon in dilute aqueous solutions and evaluated selectivity property of the sorbent in various mixture solutions. The sorption characteristics of an activated carbon (F400) were examined using $PtCl_4$ as a Pt precursor. Polyethyleneimine (PEI) was introduced on the surface of the F400 as a dispersing agent of the F400. The F400 showed an increase in the adsorption amount of Pt(IV)

by ca. 7% when it was coated with a 2.5 wt% PEI in 20 ppm of Pt(IV) solutions at pH = 4.0 The adsorption isotherms of Pt(IV) on the PEI-coated F400 which has relatively higher dispersion characteristics in an aqueous solution, when compared with pure F400, were analyzed using various isotherm models including the Langmuir isotherm models. It was found that the adsorption of Pt(IV) onto the PEI-coated F400 follows the Langmuir isotherm model. Especially, the CMPEI-coated F400 showed the best adsorption selectivity for Cu(II).

Acknowledgements

We acknowledge the financial support of Nuclear Development Fund from Ministry of Science and Technology.

REFERENCES

- [1] K. W. Park, J. H. Choi, B. K. Kwon, S. A. Lee, Y. E. Sung, H. Y. Ha, S. A. Hong, H. Kim, and A. Wieckowski, Chemical and Electronic Effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy Nanoparticles in Methanol Electrooxidation, *J. Phys. Chem. B* Vol. 106, p. 1869, 2002
- [2] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, and D. P. Wilkinson, a Review of Anode Catalysis in the Direct Methanol Fuel Cell, *J. Power Sources*, Vol. 155, p. 95, 2006
- [3] G. Che, B. B. Lakshmi, C. R. Martin, and E. R. Fisher, Metal-Nanocluster-Filled Carbon Nanotubes: Catalytic Properties and Possible Applications in Electrochemical Energy Storage and Production, *Langmuir*, Vol. 15, p. 750, 1999.
- [4] H. Tang, J. H. Chen, Z. P. Huang, D. Z. Wang, Z. F. Ren, L. H. Nie, Y. F. Kuang, and S. Z. Yao, High Dispersion and Electrocatalytic Properties of Platinum on Well-Aligned Carbon Nanotube Arrays, *Carbon*, Vol. 42, p. 191, 2004.
- [5] Y. S. Ho, Removal of Copper Ions from Aqueous Solution by Tree Fern, *Water Res.*, Vol. 37, p. 2323, 2003.