

# Electrosorption of U(VI) by Electrochemically Modified Activated Carbon Fibers

Chong-Hun Jung<sup>▲</sup>, Won-Zin Oh, Yu-Ri Lee and Soo-Jin Park<sup>1</sup>

Decontamination & Decommissioning Technology R&D Division, Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon 305-600, Korea

<sup>1</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Korea

<sup>▲</sup>e-mail: [nchjung@kaeri.re.kr](mailto:nchjung@kaeri.re.kr)

(Received December 16, 2004; Accepted January 6, 2005)

---

## Abstract

The electrosorption of U(VI) from waste water was carried out by using an activated carbon fiber (ACF) felt electrode in a continuous electrosorption cell. In order to enhance the electrosorption capacity at a lower potential, the ACF was electrochemically modified in an acidic and a basic solution. Pore structure and functional groups of the electrochemically modified ACF were examined, and the effects of the modification conditions were studied for the adsorption of U(VI). Specific surface area of all the ACFs was decreased by this modification. The amount of the acidic functional groups decreased with a basic modification, while the amount increased a lot with an acidic modification. The electrosorption capacity of U(VI) decreased on the acid modified electrode due to the shielding effect of the acidic functional groups. The base modified electrode enhanced the capacity due to a reduction of the acidic functional groups. The electrosorption amount of U(VI) on the base modified electrode at  $-0.3$  V corresponds to that of the as-received ACF electrode at  $-0.9$  V. Such a good adsorption capacity was due to a reduction of the shielding effect and an increase of the hydroxyl ions in the electric double layer on the ACF surface by the application of negative potential.

**Keywords :** *Electrosorption, Activated carbon fiber, Uranium ion, Electrochemical modification*

---

## 1. Introduction

For the removal and recovery of uranium(VI) from contaminated water and waste streams, a variety of physical and chemical methods such as precipitation, coagulation, ion exchange and adsorption have been used. But, these techniques have been restricted in application due to their limited capacity when the concentration of U(VI) in the waste water is relatively high [1-3]. As an efficient electrochemical method for the removal of a high concentration of uranium, an electrodeposition on carbon materials has been extensively investigated and used very effectively. For a uranium having a high reduction potential, electrodeposition is not a practical method [4]. An alternative to electrodeposition is electrosorption, that is an adsorption of the metal cations onto a negatively charged carbon surface [5].

The electrosorption technique, which may use the electrical potential as the 3<sup>rd</sup> driving force to the traditional adsorption and ion exchange mechanism, has the reversible characteristics of purifying a waste solution by adsorption and a concentration of the contaminants by desorption. The amount of material adsorbed in an electrosorption depends on the electrochemical potential applied to the adsorbent. When the electric potential is loaded, the electric double layer generated at the surface of the electrode is charged or discharged. By using this phenomenon, electrosorption can

be accomplished. The adsorption of ionic species or non-ionic species in a solution is influenced by the electric properties of the electrode materials. Therefore, the adsorption capacity can be controlled.

The selection of a proper electrode for an efficient removal of the trace components from a solution is very important in the design of an electrochemical system. The basic requirements for an efficient electrode material are the chemical and electrochemical inertness for a wide variety of chemicals and a wide range of potentials; high specific area (to achieve this requirement the electrode should be porous and the pores should be accessible by the electrochemically active species); high fluid permeability of the pore system; easily shaped for cell design considerations; high electronic conductivity and a continuity of the electronic contact throughout the electrode bed; and it should be cost effective [6]. Carbon-based materials (activated carbon and activated carbon fiber etc.) satisfy the requirements described above and have a good radiation and chemical resistance [7]. Activated carbons are widely used to irreversibly remove trace amounts of heavy metallic ions, transition ions and for a number of technological and analytical applications, such as a precious metal enrichment and the purification of water. Especially, activated carbon fiber (ACF), which can be easily made into a variety of types (textures or sheet), has a high specific surface area and good fluid permeability [8]. Many studies

have shown that it is possible to remove trace amounts of metallic ions such as copper, lead, zinc, cadmium, mercury and chromium.

In this study, we conducted experiments on the selective adsorption of uranium(VI) from a high concentration chemical salts. In order to enhance the electroadsorption capacity at a lower potential, the ACF felt was electrochemically modified in an acidic and a basic solution. The changes of the physico-chemical properties of the modified ACFs are investigated in terms of the BET specific surface area, total acidity and oxide functional groups by changing the treatment conditions. The adsorption behavior was obtained by varying applied potential. The results were compared with those of the adsorption behavior when the potential is not applied.

## 2. Experimental

### 2.1. Electroadsorption electrode and reagents

The electroadsorption electrode used in this study was pitch-based ACF felts (Osaka Gas Co., FN-200PS-15) with a thickness of 4~6 mm (namely, R-ACF).

The electrochemical modification was performed in a continuous system, where the ACFs were fixed over a graphite anode roller. A graphite plate cathode was also submerged in 10 wt%  $\text{H}_3\text{PO}_4$  electrolyte solution (namely, A-ACF), or 10 wt% NaOH electrolyte solution (namely, B-ACF). The conditions of the surface modifications are listed in Table 1. The modified ACFs emerging from the electrolytic cell are placed in a hot dryer oven at 110 °C for 24 h.

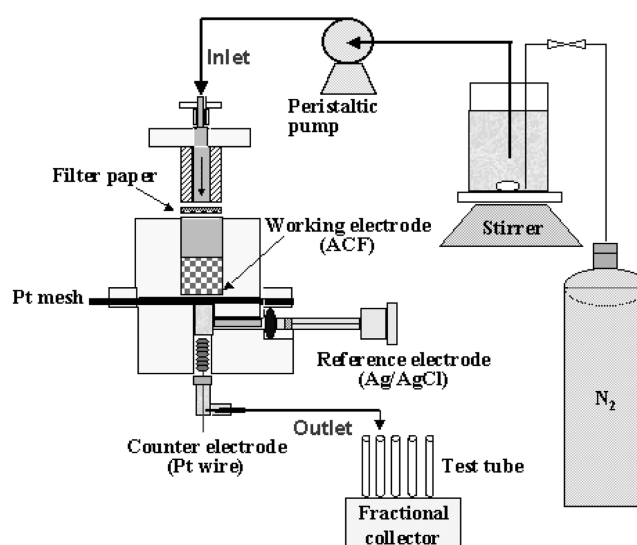
Uranium solutions were prepared by diluting a concentrated  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution with sodium nitrate and deionized water (over  $16\text{M}\Omega\text{-cm}$ ). 1 M  $\text{NaNO}_3$  was used as the supporting electrolyte solution and the concentration of the uranium nitrate was 0.05 mM. The pH of the solution was adjusted by adding 0.1 M NaOH and/or 0.1 M HCl as required. The solutions of U(VI) were purged by nitrogen gas for 40 min prior to the experiments because of the easy reduction of the dissolved oxygen in the solution.

### 2.2. Electrochemical cell

Flow-through adsorption experiments were carried out using a three-electrode electrochemical cell as shown in Fig.

**Table 1.** Experimental conditions of electrochemical modification for ACFs

Type & concentration of electrolytes	A-ACF : 10 wt% $\text{H}_3\text{PO}_4$ B-ACF : 10 wt% NaOH
Temperature (°C)	25
Current intensities (A)	1.0
Modification time (min)	1.0



**Fig. 1.** Schematic diagram of continuous flow-through cell.

1. The electric current flows parallel to the solution flow. ACF felts used as the working electrode were placed on a platinum mesh which was used as a current collector and ACF supporter. The counter electrode was platinum wire and an Ag/AgCl electrode was used as the reference electrode. All the potentials reported in this paper are relative to this reference electrode. The electrochemical cell was connected with a potentiostat (Radiometer, PGP201). The fixed flow-rates through the cell were controlled by a peristaltic pump. The effluent from the electrochemical cell was collected in a fractional collector and analyzed by a UV spectroscope (Cecil Instruments, CE2021). The adsorption behavior was investigated at various applied potentials and it was compared with the adsorption behavior of the OCP (open circuit potential).

## 3. Results and Discussion

### 3.1. Surface property of the ACF electrode

An understanding of the porosity and specific surface area of an adsorbent can be achieved by the construction of an adsorption isotherm of  $\text{N}_2$  using a gas sorption system (Quantachrome, Autosorb-1 MP). Prior to analysis, the adsorbent samples were degassed at 473 K for 12 h to obtain a residual pressure of less than  $10^{-5}$  Torr. The adsorption isotherm of the adsorbent is measured in the range of  $10^{-3}$ - $10^0$  Torr at 77 K. A relative pressure of 0.05, 0.1 and 0.15 were chosen for multipoint surface area determination. The total pore volume was derived from the amount of nitrogen vapor adsorbed at a relative pressure of about 1.0, by assuming that the pores are then filled with liquid adsorbate. The micropore volume was calculated using the t-plot method. Fig. 2 shows the  $\text{N}_2$  isotherms for the as-received

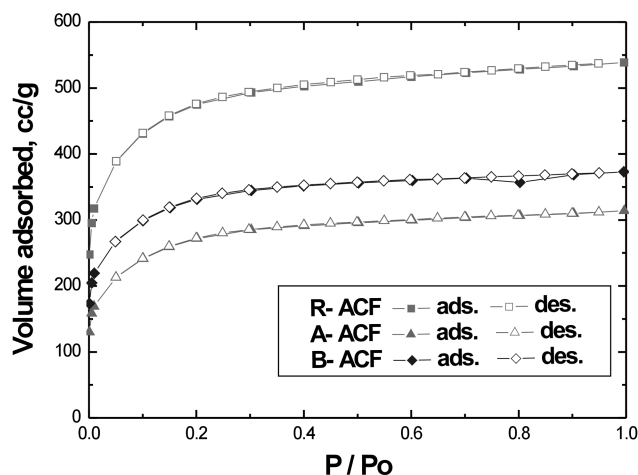


Fig. 2. Adsorption isotherms of  $N_2$  at 77 K on ACFs.

Table 2. Porosity and specific surface areas in ACFs by  $N_2$  isotherms

	$S_{BET}$ ( $m^2/g$ )	$V_{tot}$ ( $cc/g$ )	$V_{mic}$ ( $cc/g$ )
R-ACF	1733	0.83	0.59
A-ACF	998	0.48	0.31
B-ACF	1211	0.58	0.39

and the electrochemically modified ACFs, and the textural properties from the BET equation are listed in Table 2. Their shapes, as seen in Fig. 2, indicate that the pore structures are approximately type I, according to the BET classification. It is evident that most of the pore volume of the samples is filled below a relative pressure of about 0.1, indicating that these samples are highly microporous. However, the specific surface area of the ACFs are decreased by the electrochemical modification. Kutics [9] reported that the BET surface area is considerably decreased due to a blocking of the narrow pores by the surface complexes introduced by an acid treatment. Pittman *et al.* [10] found that the BET surface areas were substantially smaller than those obtained by a methylene blue and NaOH uptake, and this difference was caused by the pores, voids and cracks which can partially open or swell in the presence of aqueous base. In this study, the isotherms and porosities of the modified ACFs ensured that some of the pores were blocked by the oxide functional groups introduced by the electrochemical modification. The decrease of the surface area was mainly ascribed to the decrease of the micropore volume.

For a reasonable study of the functional groups, the titration method was used and the results are shown in Table 3. It indicates that the A-ACF produces a lot of acidic surface groups and this leads to an increase in the amount of the base required to neutralize the oxidized carbon. On the other hand, the B-ACF resulted in a decrease of the carboxyl surface groups. It is clear that the chemical nature of surface

Table 3. Surface acidity of the ACFs

	Functional group (meq/g)			Total acidity (meq/g)
	carboxyl	lactone	phenol	
R-ACF	0.32	1.30	0.84	2.46
A-ACF	2.35	1.64	1.50	5.49
B-ACF	0.01	0.27	0.32	0.60

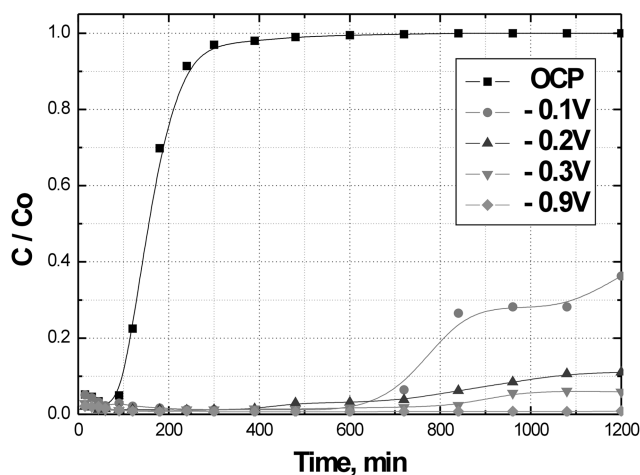


Fig. 3. Electrosorption of U(VI) with a variation of the potential at pH 4.

functionality is significantly altered by the phosphoric acid and odium hydroxide modification.

### 3.2. Electrosorption of U(VI) on a as-received ACF

A test for the electrosorption with a 100 mg/L U(VI) feed on to the R-ACF at various negative potentials in the range of  $-0.1$  to  $-0.9$  V(vs. Ag/AgCl) was carried out. The uranium concentration in the effluent from this test is shown in Fig. 3. Effective U(VI) removal is accomplished at all the negative potentials. At a potential of  $-0.3$  V, the U(VI) concentration in the effluent is reduced to 1 mg/L in 2 h and then increased continuously thereafter. At a potential of  $-0.9$  V, a complete removal (99.8%) of U(VI) is rapidly reached in 1h and maintained throughout the test. However, in the case of OCP the effluent concentration of U(VI) increased within 3h and finally reached the level of the feed, indicating a saturation of the sorption capacity by the ACF. From these results, it can be confirmed that the external negative potential exerted on the ACF electrode has a great impact on the adsorption capacity of the ACF.

The above results are replotted in Fig. 4, to examine the kinetics of the uranium sorption. The specific sorption rate can be obtained from the cumulative uranium sorption divided by the time interval and by the weight of the activated carbon fiber. At OCP, the rate of uranium sorption starts at 0.12 mg/g-min and decreases with time, approaching zero within 3h. It represents a typical adsorption break-through

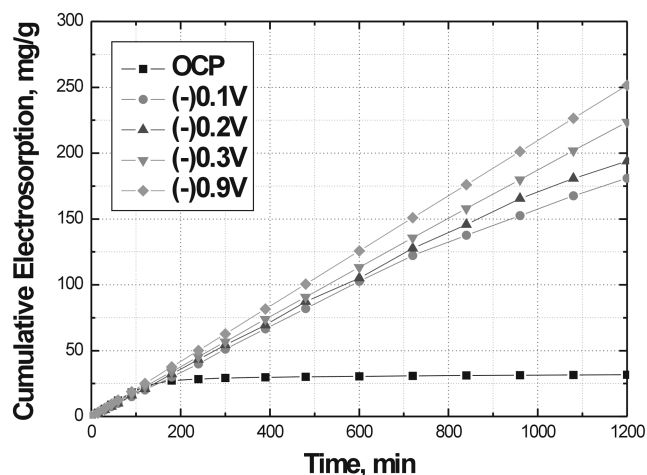


Fig. 4. Cumulative electroadsorption of U(VI) with a variation of the potential.

curve in which a saturation occurs. When the potential is  $-0.3$  V or more negative, the cumulative uranium adsorption plots are essentially straight lines, indicating a constant specific sorption rate within the time of the test. An extension of the constant sorption rates can be expected over a longer time. It is clear that the magnitude of the negative potential applied to the carbon electrode controls the uranium, sorption rate. In a test conducted with a  $100$  mg/L U(VI) feed at  $-0.9$  V, the cumulative uranium amount within 20 h is about  $252$  mg uranium / g carbon. The effluent concentration is maintained at less than  $1$  mg/L, corresponding to a specific adsorption rate of about  $195$  mg/g·min.

The capacity for U(VI) calculated at various potentials is represented in Table 4. The difference of the amount adsorbed in the OCP and the applied potential is  $159$  mg uranium / g carbon. Apparently, the external negative potential exerted on the activated carbon fiber has an impact on the adsorption capacity of the carbon fiber. The increase of the adsorption capacity for a cation is due to the electrostatic attraction by Coulomb's interaction. Many researchers have reported that the adsorption capacity of a carbon-based material was increased by an applied potential [7, 13].

### 3.3. Electrodesorption of U(VI) on a electrochemically modified ACF

In order to enhance the electroadsorption capacity at a lower potential, the ACF felt was electrochemically modified in an acidic and a basic solution.

Fig. 5 shows the electroadsorption of U(VI) with a variation of the potential on A-ACF. There are a few reports that the

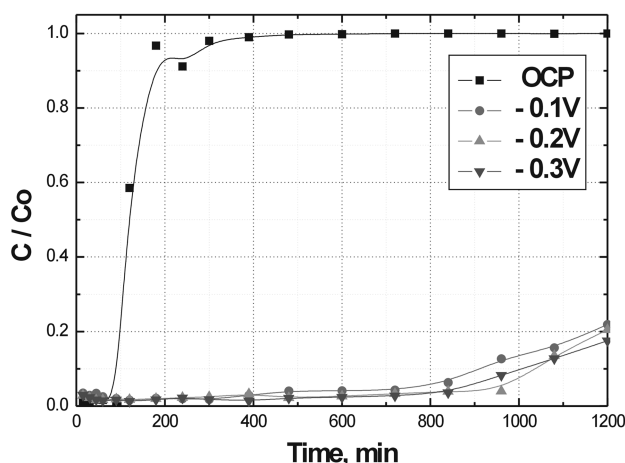


Fig. 5. Electrodesorption of U(VI) with a variation of potential on A-ACF.

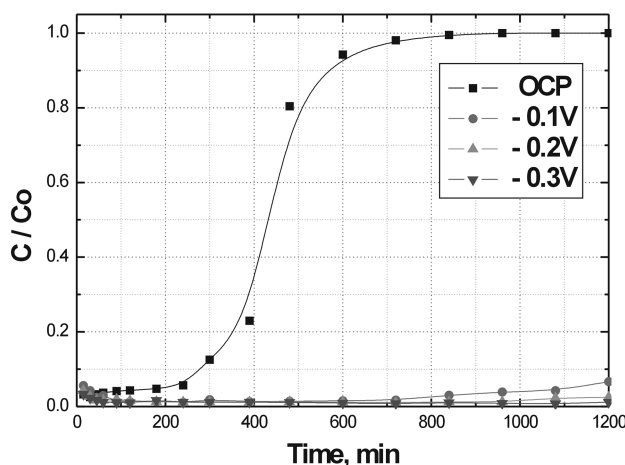


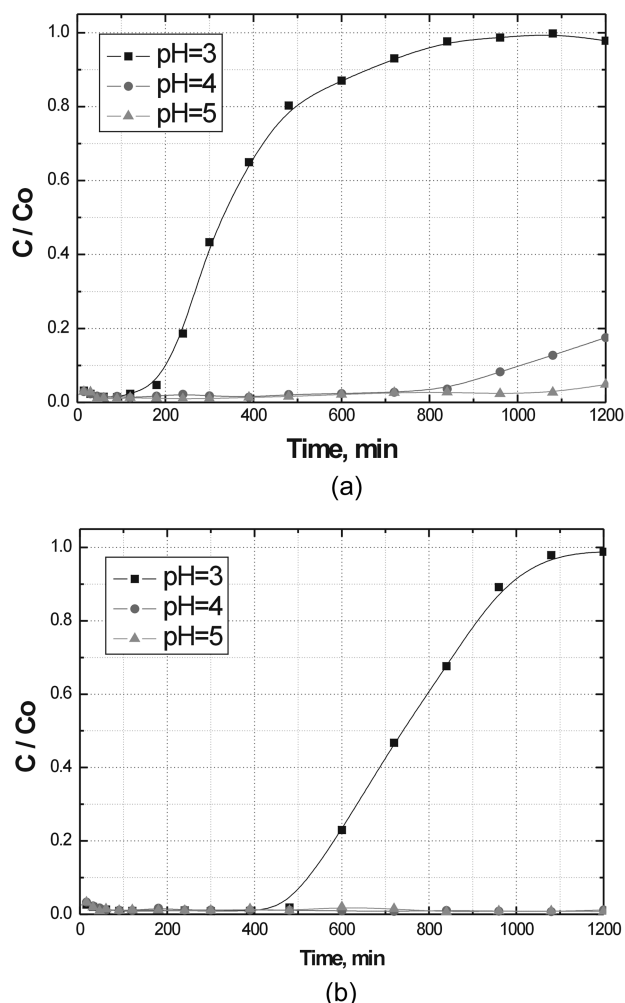
Fig. 6. Electrodesorption of U(VI) with a variation of potential on B-ACF.

functional groups of an acid modification of ACF worked as adsorption sites, enhancing its adsorption capacity [11]. Despite the functional groups increase the capacity decreased when the potential was applied and OCP, probably due to the shielding effect of the functional groups [12]. Adsorption amount of A-ACF decreases by about 10% when compared with those of the R-ACF at  $-0.3$  V. Also effluent concentration is not maintained at  $1$  ppm or less throughout the test.

Fig. 6. shows the electroadsorption of the U(VI) with a variation of the potential on B-ACF. The electroadsorption capacity of U(VI) decreased by using the A-ACF electrode while it was greatly increased by using the B-ACF electrode. At a potential of  $-0.3$  V, the U(VI) concentration in the

Table 4. Electrodesorption capacity of U(VI) with R-ACF

Applied potential (vs. Ag/AgCl)	OCP	$-0.1$ V	$-0.2$ V	$-0.3$ V	$-0.9$ V
Amount of adsorbed (mg uranium / g carbon)	21	180	193	223	252



**Fig. 7.** Electrosorption of U(VI) with a variation of solution pH on electrochemically modified ACFs; (a) A-ACF, (b) B-ACF.

effluent solution is reduced to 0.8 mg/l in 60 min. This corresponds to a 99.9% removal of U(VI) from the feed. The U(VI) concentration remains at less than 1 mg/l during the next hour of testing. The electrosorption amount of U(VI) on the B-ACF electrode at  $-0.3$  V corresponds to that of the R-ACF electrode at  $-0.9$  V. Such a good adsorption capacity was not only due to a reduction of the shielding effect but also to an increase of the hydroxyl ions in the electric double layer on the ACF surface by the application of a negative potential.

From these results, the electrosorption capacity is affected by a surface acidity more than the specific surface area. It can be confirmed that the electrosorption of U(VI) depends on the chemical property of the electrode.

For the electrosorption tests shown above, the pH of the influent was maintained at 4.0. To examine the effects of solution pH on the uranium removal, more tests were run at a potential of  $-0.3$  V and influent pH of 3.0 and 5.0, respectively.

Fig. 7 shows the electrosorption of U(VI) with a variation of the pH on electrochemically modified ACFs at  $-0.3$  V. As the solution pH was lowered, the amount of U(VI) adsorbed on A-ACF decreased. This is similar to an ion-exchange sorption where the adverse effects of a low pH on the cation sorption are always observed. At pH 3.0, the effluent U(VI) concentration rapidly increases at about 1.5h, yielding an extremely low uranium sorption capacity. The electrosorption at pH 4.0 and 5.0 shows very similar results except for a higher uranium removal after 14 hr of the electrosorption at pH 5.0. Also, the B-ACF shows a sorption capacity better than the A-ACF throughout the test.

#### 4. Conclusion

The electrosorption of U(VI) from waste water was carried out by using an activated carbon fiber (ACF) felt electrode in a continuous electrosorption cell. The applied negative potential increased the adsorption kinetics and capacity in comparison to an open circuit potential (OCP) adsorption for uranium ions. The electrosorption amount of U(VI) on the base modified ACF electrode at  $-0.3$  V corresponds to that of the as-received ACF electrode at  $-0.9$  V. Such a good adsorption capacity on the base modified ACF electrode at less negative potential was not only due to a reduction of the shielding effect of the acidic functional groups on the ACF surface but also to an increase of the hydroxyl ions in the electric double layer on the ACF surface by the application of a negative potential.

#### Acknowledgment

This work has been carried out under the Nuclear R&D program by MOST.

#### References

- [1] Sauer, N. N.; Smith, B. F. *Metal-Ion Recycle Technology for Metal Electro-Plating Waste Waters*; LA-12532-MS, **1993**.
- [2] Oren, Y.; Soffer, A. *J. App. Electrochem.* **1983**, *13*, 473.
- [3] Jayson, G. G.; Sangster, J. A.; Thompson, G.; Wilkinson, M. C. *Carbon* **1987**, *25*, 523.
- [4] Carley-Macaulay, K. W.; Gutman, R. G. *Radioactive Waste: Advanced Management Methods for Medium Active Liquid Waste*; Harwood Academic Pub., **1981**.
- [5] Woodard, F. E.; McMackins, D. E.; Jansson, R. E. W. *J. Electroanal. Chem.* **1986**, *214*, 303.
- [6] Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H., *Surface Tension and Adsorption*; Longmans, London, **1980**, 218.

- [7] Tomizuka, I.; Meguro, T.; Kuwagaki, H.; Chiba, A.; Miyazaki, A.; Okamoto, M. Proceeding of Carbon '94, Granada, Spain, **1994**, 222.
- [8] Hatfield, T. L.; Kleven, T. L.; Pierce, D. T. *J. Appl. Electrochem.* **1996**, 26, 567.
- [9] Kutics, K.; Suzuki, M. 2<sup>nd</sup> Korea-Japan Symposium on Sep. Tech., Seoul, South Korea, **1990**, 395.
- [10] Jr Pittman, C. U.; He, G. R.; Wu, B.; Gardner, S. D. *Carbon* **1997**, 35, 317.
- [11] Park, S. J.; Kim, Y. M.; Shim, J. S. *J. Korean Ind. Eng. Chem.* **2004**, 14, 41.
- [12] Takamura, T.; Awano, H.; Ura, T.; Ikezawa, Y. 36th Battery Sym., Japan, **1995**, 92.
- [13] Niu, J., Conway, B. E. *Journal of Electroanalytical Chemistry* **2002**, 536, 83.