# Diamond and Platinum Electrodes For Urea Electrochemical Oxidation

N.A. Bazaev, B.M. Putrya, Ye.V. Streltsov

National Research University of Electronic Technology. Shokin Square 1, Zelenograd, Russia
Contact: PutryaBM@gmail.com

## Introduction

Dialysate regeneration process can be potentially used in wearable artificial kidney (WAK) development as a method of uremic toxins removal [1–3]. These toxins and metabolites include nitrogen-bound substrates (urea, uric acid, creatinine etc), aromatic substrates (such as p-cresol), phosphates, nitrates etc. For purpose of dialysate regeneration the following approaches can be used: sorbent method [4], electrochemical method [5, 6], enzymatic method [7] etc. Each of them has its own advantages and disadvantages and overall different combinations of methods listed above can be used for effective dialysate regeneration. Nitrogen-bound substrates removal is one of the main issues of dialysate regeneration. While sorbents can effectively remove creatinine and uric acid, they are not effective in case of urea elimination. Thus alternative solution has to be found. In this paper urea electrochemical oxidation on diamond and platinum electrodes was investigated.

This paper is dedicated to electrochemical urea oxidation method. All experiments were performed in acidified solution (pH = 5.4). The following reactions might take place on anode and cathode surfaces and in the solution during electrolysis of acidified solution:

| Cathode: | Anode: |
|---|---|
| $H^+$, $Ca^{2+}$, $Na^+$, $Mg^{2+}$, $Cl^-$, $H_2O$ | $(NH_2)_2CO$, $H_2O$, $Cl^-$ |
| Reduction of $H^+$ and water | Oxidation of urea, $Cl^-$ and water |

| | | | |
|---|---|---|---|
| C | 3 | $2H^+ + 2e^- = H_2\uparrow$<br>$2H_2O + 2e^- = H_2\uparrow + 2OH^-$ | $+ 4e^-$ |
| A | 1 | $(NH_2)_2CO + H_2O - 6e^- = N_2\uparrow + CO_2\uparrow + 6H^+$<br>$2Cl^- - 2e^- = Cl_2\uparrow$<br>$2H_2O - 4e^- = O_2\uparrow + 4H^+$ | $- 12e^-$ |

Molecular formula for anode urea oxidation:

$(NH_2)_2CO + 3H_2O + 2HCl = 6H_2\uparrow + N_2\uparrow + CO_2\uparrow + O_2\uparrow + Cl_2\uparrow$

The following reaction might take place in the solution:

$$\overset{0}{Cl_2} + H_2O = \overset{+1}{H}\overset{}{Cl}O + \overset{-1}{H}\overset{}{Cl}$$

Urea hydrolysis in acidified medium can be presented by the following reaction:

$$(NH_2)_2CO + 2H^+ + H_2O = 2NH_4^+ + CO_2\uparrow$$

$$(NH_2)_2CO + 2HCl + H_2O = 2NH_4Cl + CO_2\uparrow$$

Urea reduction can also take place due to urea's reaction with atomic hydrogen during its generation on cathode surface:

$$2\overset{0}{H} + (\overset{-3}{N}H_2)_2\overset{+4}{C}O + 2H_2O = \overset{+2}{C}O\uparrow + 2NH_3\cdot\overset{+1}{H}_2O$$

Urea oxidation can take place in the solution due to its reaction with hypochlorous acid:

$$(\overset{-3}{N}H_2)_2CO + 3H\overset{+1}{C}lO = \overset{0}{N}_2\uparrow + 3H\overset{-1}{C}l + CO_2\uparrow + 2H_2O$$

It should be emphasized that during urea electrochemical oxidation different toxic byproducts (including sodium hypochlorite) are generated and accumulated in the solution. To resolve this problem different types of materials can be used including ion-exchange resins and non-selective sorbents such as activated carbon.

## Materials and Methods

In this work dialysate regeneration by means of electrochemical oxidation method has been investigated. Effectiveness of electrochemical dialysate regeneration depends on multiple factors, such as initial ion composition of dialysate solution, initial concentration of nitrogen-bond substrates, pH of solution, solution initial temperature, current density, electrode surface, electrode material etc [8–13]. In this article all experiments were performed in a solution for peritoneal dialysis Fresenius Balance (glucose 1.5 %). Initial pH of the solution was 5.4. The solution contains glucose as an osmotic agent (glucose concentration – 1.5%). Composition of the solution is presented in table 1.

**Table 1:** Fresenius Balance (glucose 1.5 %)

| Ion | Concentration, mmol/l |
|---|---|
| Calcium ($Ca^{++}$) | 1,75 |
| Sodium ($Na^+$) | 134,0 |
| Magnesium ($Mg^{++}$) | 0,5 |
| Chloride ($Cl^-$) | 103,5 |

The model solution contained 30 mmol $l^{-1}$ of urea. Solution was recirculated through hermetic electrochemical cell with rate 50 ml/min. Cumulative anode surface for each electrode type was 150 $cm^2$. The volume of the model solution was 500 ml.

The following electrode types were chosen for experiment: smooth-platinum films deposited on titanium sub-

strate and boron-doped diamond films deposited on titanium substrate.

Preliminary cyclic voltammetry (CV) for electrode samples was studied. Experimental three-electrode cell for CV is presented on figure 1.

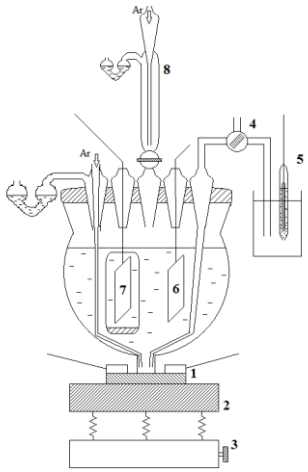


**Figure 1:** Three-electrode experimental cell for CV studies: 1 – electrode sample; 2 –table; 3 – lifting mechanism; 4 – salt bridge; 5 – reference electrode Ag/AgCl; 6, 7 – auxiliary electrodes; 8 – argon purge system

Cell top had five polished outlets for electrodes and argon flow system. Auxiliary electrode was separated from anode space with glass filter. Argon gas to provide inert medium inside the system was circulating through electrochemical cell. Reference electrode Ag/AgCl was linked to worked electrode through salt bridge filled with saturated solution of potassium chloride.

Experimental set-up is presented on figure 2.

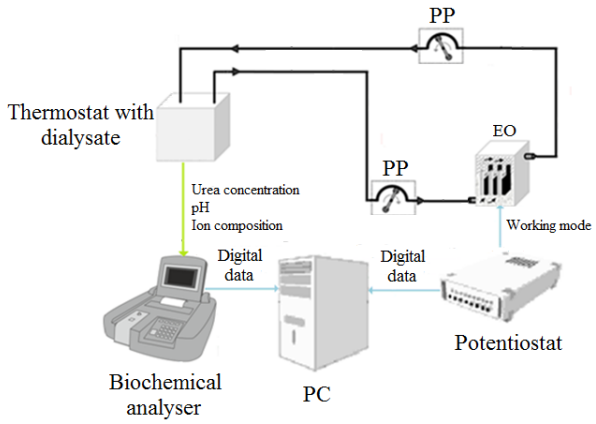


**Figure 2:** Experimental set-up for electrode samples testing: PP – peristaltic pump; EO – electro-oxidation cell

Urea concentration, pH and ion composition of the solution were controlled on biochemical analyzer Stat Fax 3300. Potentionstat PI-50-Pro controlled electrochemical cell working mode. All gathered data was processed and stored on personal computer. 1 ml of dialysate sample was taken every hour for urea and pH concentration measurement. Current density was 5 mA $cm^{-2}$.

## Results

Cyclic voltammetries for platinum and diamond electrodes were studied.

Figures 3 and 4 present the cyclic voltammetries obtained with diamond and Pt electrodes in the solution for peritoneal dialysis with a scan rate of 10 mV $s^{-1}$ for different urea concentrations.

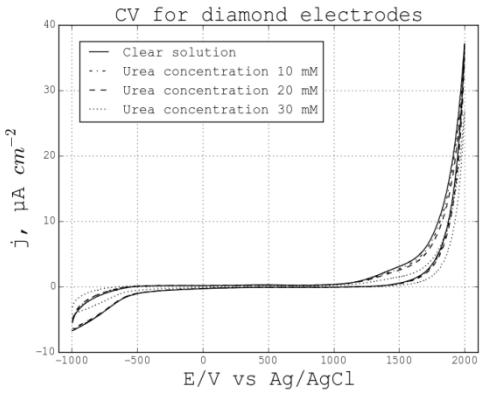


**Figure 3.** Cyclic voltammetry obtained with diamond electrode in the solution for peritoneal dialysis (Fresenius) for different urea concentrations (scan rate – 10 mV $s^{-1}$)

In case of diamond electrodes, the presence of urea decreases current density in potential regions from -1000 to -500 mV vs Ag/AgCl and from 1000 to 2000 mV vs Ag/AgCl.

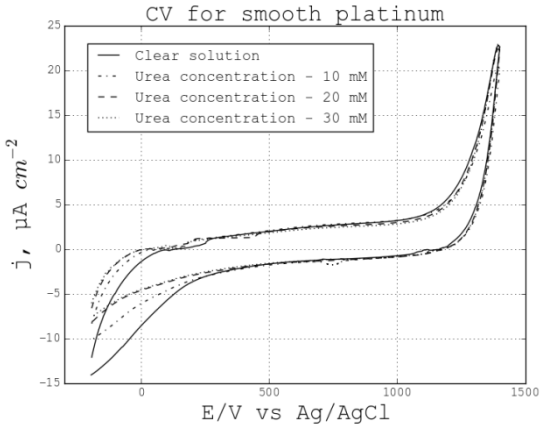


**Figure 4.** Cyclic voltammetry obtained with smooth platinum electrode in the solution for peritoneal dialysis (Fresenius) for different urea concentrations (scan rate – 10 mV $s^{-1}$)

In case of cyclic voltammetry for smooth platinum electrode urea presence also altered the curve shape. Urea presence changed current density in the potential regions from -400 to 200 mV vs Ag/AgCl. At the same time, no current density change was observed on potential region from 1100 to 1400 mV vs Ag/AgCl. Observed phenomenon on both electrodes can be explained by electrode surface blockage due to urea adsorption on electrodes.

In the next stage urea oxidation rate for different electrode types was studied. Diamond and Ti/Pt electrodes were selected for this purpose. The main results of the experiment are presented on fig. 5.

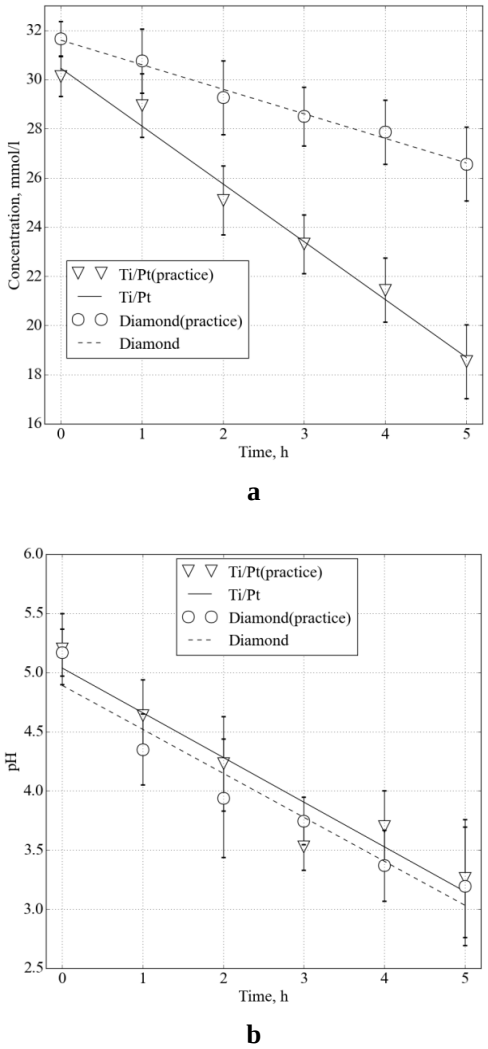


**Figure 5.** Results of experiment: a) urea concentration as a function of time; b) pH as a function of time

For Ti/Pt electrode urea oxidation rate was 69.54±4.3 mg $h^{-1}$, while for boron-doped diamond electrodes - 30.60±4.1 mg $h^{-1}$. The fact that platinum electrodes had higher urea elimination rate in comparison with diamond can be explained by catalytic properties of platinum.

Both diamond and platinum electrodes decreased pH of dialysate from 5.2 to 3.2. Increase of chloride was observed for both electrode samples. The highest chloride increase rate was observed for platinum electrodes (5±1 mM $h^{-1}$). For diamond electrodes chloride the increase rate was 2±1 mM $h^{-1}$. Ti/Pt produced 0.142±0.02 mg of sodium hypochlorite during the experiment, while sodium hypochlorite production was not observed for diamond electrodes.

## Discussion

Cyclic voltammetries for both platinum and diamond electrodes in the solution for peritoneal dialysis have shown the tendency of urea to be adsorbed by electrode surface, which led to decrease of current density and change of the curve shape. At the same time, it was impossible to estimate what anode potential was preferable for potentiostatic urea oxidation. According to [14] experiments of potentiostatic urea oxidation mode demonstrated that this mode was ineffective due to low reaction kinetics. During the experiment, low urea oxidation rate was observed.

Galvanostatic urea-oxidation mode proved more effective than galvanostatic mode; however, it affected solution ion composition and pH and increased sodium hypochlorite generation in case of Ti/Pt. It is remarkably that hypochlorite generation was not observed for diamond electrodes. It should be also noted that ion chloride concentration increase on diamond was less intense in comparison with Ti/Pt, although diamond acidified solution with the same rate as platinum. These properties could possibly compensate low urea-oxidation rate; however, diamond electrodes were not stable and degraded during electrolysis due to high current density (5 mA $cm^{-2}$), which excluded diamond electrodes as a candidate for dialysate regeneration.

Ti/Pt electrodes was approved as more stable material with higher urea oxidation rate, but high sodium hypochloride generation rate, electrolysis influence on ion composition and pH of the solution should be taken into consideration. These issues can be resolved by adding ion exchange resins, activated carbon and degasser in dialysate regeneration unit.

## Conclusions

Titanium diamond electrodes had lower oxidation rate and did not produce sodium hypochlorite, and at the same time they were unstable and dissolved during electrolysis which made this electrode type inappropriate for dialysate regeneration unit. Ti/Pt was the most stable material in case of electrolysis with higher urea oxidation rate and thus it is still the most prominent material for renal replacement therapy with regeneration.

Urea electro-oxidation on platinum electrodes may be potentially used in case of dialysate regeneration. However, pH stabilization of the solution is required. This issue can be resolved by adding activated carbon column. Future research will be warranted to investigate the possibilities of ion composition and pH control in closed-loop dialysate regeneration system during the process of urea electrochemical oxidation.

## References


[1]. Maria Jafaar. Horizon Scanning Report. Wearable Dialysis Device. // Report No: 006/2016.

[2]. A wearable artificial kidney for patients with end-stage renal disease / Gura V. [et al.] // JCI Insight. 2016. P. 1–15.

[3]. Maintenance dialysis throughout the world in years 1990 and 2010. Thomas B. [et al]. Journal of the

American Society of Nephrology. 2015. Vol. 26. №11. P/ 2631–2633.
[4]. John WM Agar. Review Understanding sorbent dialysis systems // Nephrology. 2010. Vol. 15. P.406–411.
[5]. W. Simka, J. Piotrowski, G. Nawrat. Influence of anode material on electrochemical decomposition of urea // Electrochim. Acta. 2007. Vol. 52. P.5696–5703.
[6]. Removal of urea in wearable dialysis device: a reappraisal of electro-oxidation / Maarten Wester [et al.] // Artificial Organs. 2014. P.1–17.
[7]. A wearable haemodialysis device for patients with end-stage renal failure: a pilot study / Andrew Davenport [et al.] // Lancet. 2007. Vol. 370. P. 10
[8]. J.C. Wright, A.S. Michaels, A.J. Appleby Electrooxidation of urea at the ruthenium titanium oxide electrode // AIChe J. 1986. Vol. 32. P.1450–1458.
[9]. Electrocatalytic oxidation of urea on a sintered Ni–Pt electrode / W. Simka [et al.] // J. Appl. Electrochem. 2009. Vol. 39. P.1137–1143.
[10]. B.K. Boggs, R.L. King and G.G. Botte. Urea electrolysis: direct hydrogen production from urine. Chem // Commun. 2009. Vol. 32 P.4859–4861.
[11]. A.T. Miller, B.L. Hassler, G.G. Botte. Rhodium electrodeposition on nickel electrodes used for urea electrolysis // Appl. Electrochem. 2012. Vol. 42. P. 925–934.
[12]. V. Vedharathinam, G.G. Botte. Understanding the electro-catalytic oxidation mechanism of urea on nickel electrodes in alkaline medium // Electrochim. Acta. 2012. Vol. 81. P.292–300.
[13]. V. Vedharathinam, G.G. Botte. Direct evidence of the mechanism for the electro-oxidation of urea on $Ni(OH)_2$ catalyst in alkaline medium // Electrochim. Acta. 2013. Vol.108. P.660–665.
[14]. Electrochemical Removal of Urea from Physiological Buffer as the Basis for a Regenerative Dialysis System / Richard W. Keller [et al.] // J.Electroanal. Chem. 1980. Vol. 116. P.469–485.

## Acknowledgements

This work was partly financed by the Ministry of Education and Science of the Russian Federation (project ID RFMEFI57917X0152, Contract № 14.579.21.0152, 26.09.2017).