Investigation of Changes In the Surface Chemistry and Morphology of Platinum Microelectrodes Subjected to a Dielectrophoretic Field

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Platinum microelectrodes are widely used in microdevice applications as they are considered to be inert and noncorrodible. Chemical and morphological changes that occur on platinum surfaces are well documented, and results from our laboratory suggested that platinum microelectrodes subjected to electric fields undergo changes that affect their performance. Chemical and morphological changes on platinum microelectrodes subjected to ≤ 1.5 V_{pp} and 6 V_{pp} electric fields in NaCl and KH_2PO_4/K_2HPO_4 solutions were investigated with cyclic voltammetry and scanning electron microscopy. The results show that a number of chemical and morphological changes occur on platinum surfaces over time, which may significantly affect reusability of microdevices utilizing them.

Introduction

Platinum is a popular electrode material in biological microdevice applications because it is considered to be inert and noncorrodible. As a result, platinum microelectrodes are often used to generate AC and DC electric fields in microdevices, and any electrochemical effects are largely ignored in microanalytical systems. This is a valid assumption over a limited range of voltages; platinum does not dissolve in electrolytic solutions when the applied potential is between the potentials of hydrogen and oxygen evolution [1,2]. A large number of microdevices employ electrophoretic techniques such as capillary electrophoresis (CE), and capillary zone electrophoresis [3]. Electric fields are used to facilitate electroosmotic flow in microdevices [3-5]. Electrode chemistry effects are undesirable in these applications because they rely on either AC or DC electric field effects for separation of cells and particles [3,6-10]. However, in a limited number of applications, such as isoelectric focusing, pH gradients are employed to separate cells and particles [3,11]. These pH gradients can be generated in part by hydrolysis reactions at the microelectrodes, whereby surface changes on platinum electrodes are undesirable, since they can affect the hydrolysis reactions [11]. AC fields have been touted as advantageous over DC fields on the grounds that undesirable reactions at electrode surfaces can be avoided with AC fields. This work demonstrates the fallacy of this assumption.

Chemical and physical changes that platinum electrodes can undergo in AC and DC electric fields are well documented in the electrochemistry literature and fall into five categories, namely, chemical reactions of platinum, oxide formation, dissolution of platinum, adsorption on platinum surfaces and Ostwald ripening. These mechanisms are discussed in more detail in our full paper [12].

The presence of these chemical and physical changes were investigated in conditions similar to those in currently developed microdevices. Recently in our group, platinum microelectrodes were utilized to disrupt red blood cell membranes by the application of AC electric fields; it was observed that older platinum microelectrodes ruptured the red blood cells more rapidly than newer ones [13]. This observation suggests that some properties of platinum microelectrodes change with time when they are subjected to AC electric fields, which in turn impacts electric fields in microdevices. Property changes in platinum microelectrodes would have implications for analytical microdevices, because changes in the electric field can affect the behavior of cells by changing the speed of electrophoretic separations or electric field gradients. It is desirable to understand the chemical and morphological changes that platinum microelectrodes undergo and determine the conditions (frequency, potential, etc.) under which microdevice electric fields remain reliably constant.

To this end, cyclic voltammetry (CV) has been used to determine the chemical changes that occur on platinum microelectrodes in NaCl and K_2HPO_4/KH_2PO_4 solutions. These electrolytes are the constituents of phosphate buffer saline (PBS) solution, which is commonly used in medical microdevices. The solutions used in the CV study had the same ionic strength as the PBS solution used in other studies in our lab, which mimics the salinity of human blood. CV plots obtained with NaCl and K_2HPO_4/KH_2PO_4 solutions were compared to determine the effect of chlorine on chemical and morphological changes on platinum surfaces under the experimental conditions. Morphologies of new platinum microelectrodes and those subjected to electric fields were compared by scanning electrochemical microscopy (SEM).

A more complete surface chemical analysis of platinum microelectrodes under AC and DC conditions can be found in our full paper, "Morphological and Chemical Changes on Platinum Microelectrode Surfaces in AC and DC Fields with Biological Buffer Solutions" [12].

Materials and Methods

Cyclic voltammetry experiments were carried out using new microelectrodes made of 0.1 mm diameter platinum wire with 99.99% purity (Goodfellow, Huntingdon, UK) as the working electrode, a 1 mm diameter platinum wire as the auxiliary electrode, and a 1 mm diameter silver wire as the quasi-reference electrode (QRE). Unbiased potential signals of 1.5 V_{pp} and 6 V_{pp} were applied, with a scan rate of 80 mV/s. CV investigation of new platinum working electrodes was carried out in NaCl solution (0.274 M NaCl) and potassium phosphate solution (PPS) (0.036 M KH_2PO_4, 0.012 M K_2HPO_4) in order to observe any reactions involving ions present in PBS solution separately.

To study the morphological changes on platinum microelectrodes using SEM, two new microelectrodes were subjected to a 2 kHz AC field in freshly prepared NaCl solution and two were subjected to a 2 kHz AC field in freshly prepared PPS solution for 5 hours. For both solutions, one of the prepared microelectrodes was subjected to an AC field potential of 1 V_{pp} and the other to a field potential of 6 V_{pp} with an electrode spacing of 175 μm for a resulting field strength of 3.43E4 V/m. All four microelectrodes were prepared with new platinum wire and fresh electrolyte solution.

SEM images were taken using a JEOL JSM-6500F field emission microscope (JEOL USA, Peabody, MA) under a vacuum of 2.72E-6 torr. All samples were energized with a 5.0

keV electron beam. The portion of surface covered by a feature was estimated by laying a 5 µm x 5 µm grid over the SEM images and comparing the number of vertices on a feature to the total number of vertices.

Results and Discussion

Cyclic voltammetry plots of platinum microelectrodes in NaCl and potassium phosphate solutions with 1.5 V_{pp} and 6 V_{pp} signals are shown in Figure 1. The surface areas of the microelectrodes were not controlled; therefore, a normalization of currents according to surface area and quantitative comparison of results were not possible. Potentials are given as "volts against silver quasi-reference electrode" (V_{AgQRE}). Only the sections from -1.25 V_{AgQRE} to 1.25 V_{AgQRE} of CV plots generated by a 6 V_{pp} signal are shown, since the currents abruptly became excessively high beyond these values. This sharp increase in the current suggests a large capacitative current, which is caused by the restructuring of the electrolyte double layer near the electrode surface and does not indicate electron transfer to or from the electrode surface. The negative sweeps revealed electrochemical oxidation peaks at -0.15 V_{AgQRE} with 1.5 V_{pp} signals and at -0.25 V_{AgQRE} with 6V_{pp} signals, while the positive sweep featured a plateau, indicating that the oxidation of platinum microelectrodes is

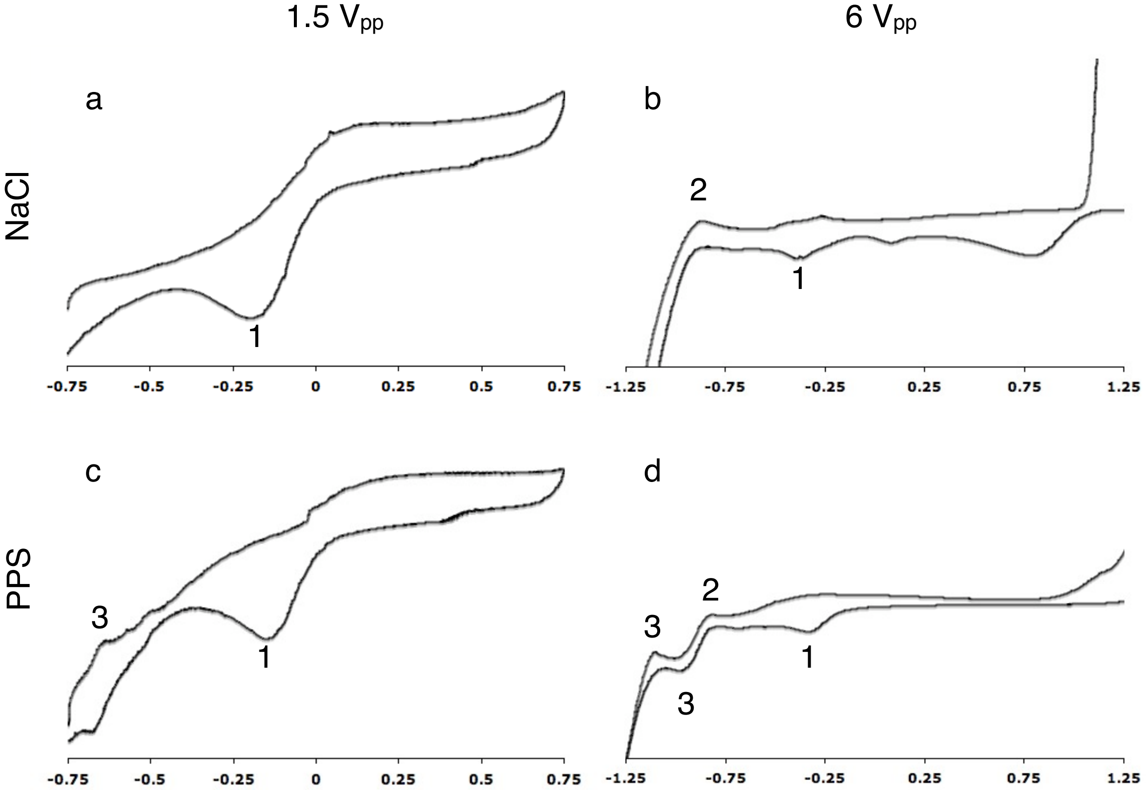

Figure 1: Cyclic voltammetry plots of platinum microelectrodes with a platinum counter electrode and a silver reference electrode at a scan rate of 80 mV/s. a) NaCl solution with a 1.5 V_{pp} signal, b) NaCl solution with a 6 V_{pp} signal, c) Potassium phosphate solution with a 1.5 V_{pp} signal, d) Potassium phosphate solution with a 6 V_{pp} signal. Features labeled on the figure indicate: 1) Electrochemical oxidation of platinum, 2) Hydrogen formation from water reduction, 3) Potassium adsorption/desorption.

irreversible. Hydrogen formation from water reduction was observed at -0.80 V_{AgQRE} with $6V_{pp}$ signals but not with 1.5 V_{pp} signals, as was expected. The current increased as the potential increased with 1.5 V_{pp} signals, suggesting an adsorption process. These results are in agreement in with a published CV investigation of platinum foil carried out in a PBS solution prepared with Na_2HPO_4, NaH_2PO_4 and NaCl, and reporting chloride and oxygen formation at higher positive potentials [14]. In the CV plots generated in our lab with potassium phosphate solution, a peak in the positive sweep was observed at a potential of -0.65 V_{AgQRE} with a 1.5 V_{pp} signal and at -1.08 V_{AgQRE} with $6V_{pp}$ a signal, suggesting potassium adsorption on the platinum microelectrode surfaces. A corresponding peak was also observed in the negative sweep at -0.97 V_{AgQRE} with a 6 V_{pp} signal. These peaks were not present in CV plots generated with NaCl solution or in the CV plots generated with a potassium-free buffer presented in another study [14]. In conclusion, CV verified that oxide formation, hydrogen formation from water reduction, chloride formation and potassium adsorption take place on the platinum microelectrode surfaces.

SEM was used to determine changes in the surface morphology of platinum microelectrodes after 5 hours in a 2 kHz, 1 V_{pp} or 6 V_{pp} AC electric field. It was found that the morphology of platinum microelectrodes changed considerably after 5 hours in an AC electric field. A comparison of new platinum microelectrodes and platinum microelectrodes

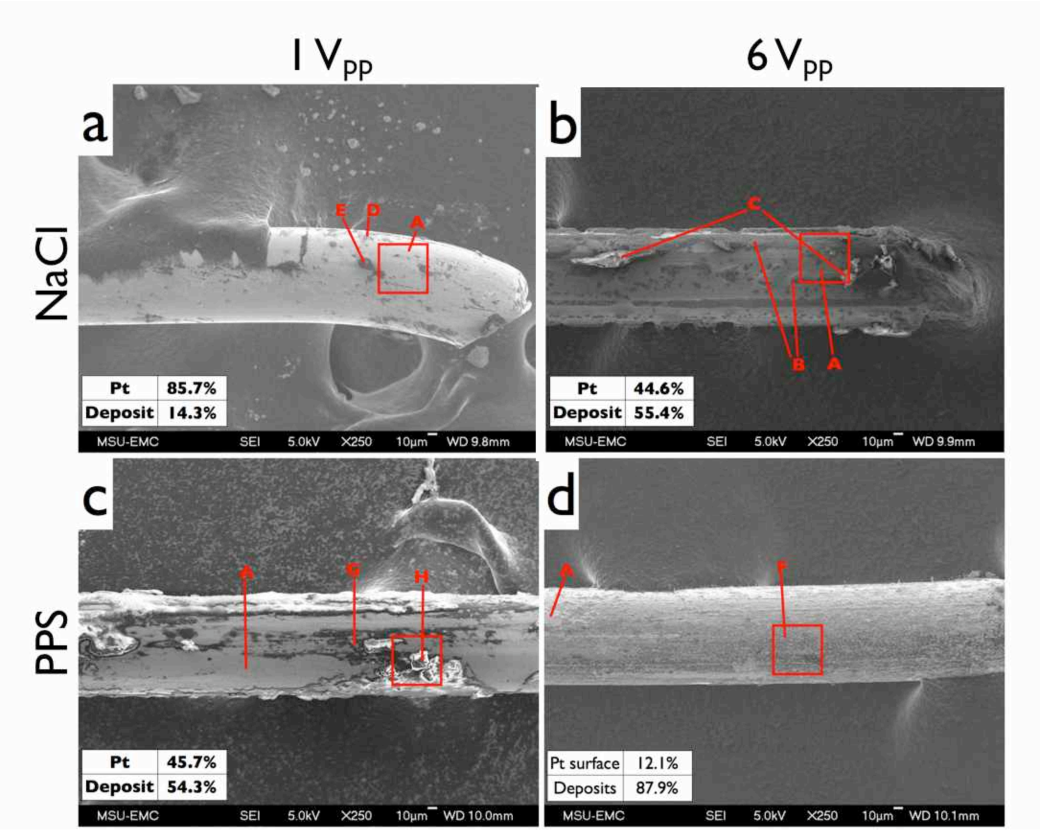

Figure 2: Scanning electron microscopy images of platinum microelectrodes at 250X magnification. Values in the lower left corner of each image give the percentage of surface area of morphological features, estimated by a 5 µm x 5 µm grid over the whole surface. a) NaCl solution with 1 Vpp signal, b) NaCl solution with 6 Vpp signal, c) Potassium phosphate solution with 1 Vpp signal, d) Potassium phosphate solution with 6 Vpp signal. Red squares indicate areas magnified in Figure 3. Red letters indicate features described in the text.

that were subjected to 1 V_{pp} and 6 V_{pp} electric fields in NaCl and potassium phosphate solutions for 5 hours is given in Figure 2, along with the percentages of surfaces that are affected by morphological changes, as estimated by application of a 5 µm x 5 µm grid over the images. Platinum surfaces affected by dissolution of platinum but otherwise free of deposits were regarded as free of morphological features in the estimation of these percentages.

The most notable features that appeared after prolonged exposure to the electric field were deposited material on the electrode surface and platinum dissolution. This effect is most pronounced in the platinum microelectrode subjected to a 6 V_{pp} electric field in NaCl solution. On this microelectrode, it was observed that large areas of the electrode surface were dissolved (Marked as A on Figure 2a), as opposed to the more localized deformations due to dissolution that were observed with the other electrode conditions. In addition, two different material deposits were observed, one consisting of large particles (Marked as B on Figure 2a) and the other consisting of layers of crystalline deposits (Marked as C on Figure 2a), the latter of which can be seen in higher magnification in Figure 3a. Material deposition (Marked as D on Fig 2b) and surface changes (Marked as E on Figure 2b) were observed on 14.3% of the microelectrode subjected to a 1 V_{pp} electric field in NaCl solution. Part of the surface of this microelectrode was obscured by material from the mounting tape and was excluded from analysis. Platinum dissolution was much less severe on the microelectrode which was subjected to a 6 V_{pp} electric field in potassium phosphate solution compared to the one subjected to the same field in NaCl solution, but 87.9% of the surface was covered with deposited material (Marked as F on Figure 2c). Surface changes (Marked as G on Figure 2d) and large areas of material deposits (Marked as H on Figure 2d) covering 54.3%

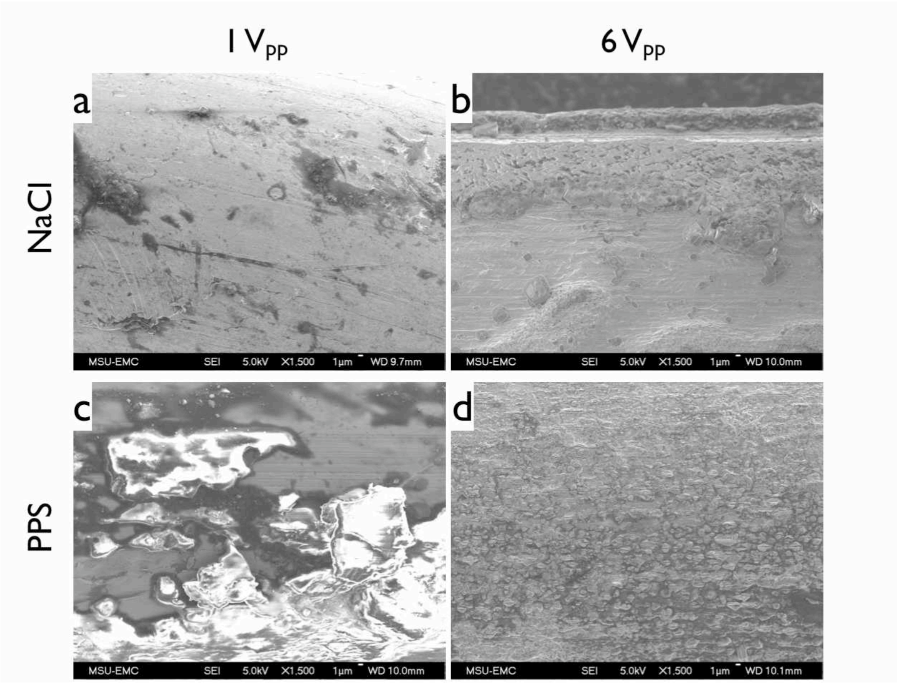

Figure 3: SEM images of red boxed features on Figure 2 at X1500 magnification. a) NaCl solution with 1 Vpp signal, b) NaCl solution with 6 Vpp signal, c) Potassium phosphate solution with 1 Vpp signal, d) Potassium phosphate solution with 6 Vpp signal.

of the microelectrode surface were observed on the microelectrode subjected to a 1 V_{pp} electric field in potassium phosphate solution. Further chemical analysis by energy dispersive spectroscopy (EDS) is presented in our full paper [12].

Images of the observed features taken at higher magnifications are shown in Figure 3. In Figure 3a, it can be seen that the platinum surface of the microelectrode subjected to a 6 V_{pp} field in NaCl solution has a rough topography compared to the smooth appearance of the other microelectrodes, further demonstrating the severity of platinum dissolution on this sample. It was observed from Figure 3a and Figure 4a and another SEM image of the sample shown in Figure 3a that in a 6 V_{pp} electric field in NaCl solution, platinum dissolution is severe enough that the overall thickness of the wire is reduced by ~10% over the 5 hour experiment. Dissolution of platinum is observed in all cases, and it is known that dissolved platinum can be redeposited on the platinum surface when the electric field is reversed, as occurs in AC applications, causing heterogenous growth of platinum crystals on the surface [15].

Conclusions

Chemical and morphological changes to platinum microelectrode surfaces subjected to 1 V_{pp}/175 μm and 6 V_{pp}/175 μm AC electric fields in chlorine-bearing and chlorine-free solutions were compared. These conditions are commonly encountered in medical microdevices. More drastic chemical and morphological changes to microelectrodes were observed in 6 V_{pp} fields as opposed to 1 V_{pp} fields. Surface changes and dissolution of platinum, as well as material deposition and the possible redeposition of platinum were observed in all cases. Results from our own laboratory suggest that these chemical and morphological changes affect the electric field produced by platinum microelectrodes and subsequent chemical analyses.

These findings point to the fact that despite its well known resistance to corrosion, platinum is susceptible to chemical and morphological changes which can potentially alter performance of medical microdevices over time and limit their reusability, as changes in the electric field mean changes in the cell responses and inconsistent behaviors. In microdevice design, the media that the microelectrodes will contact and the electric fields they will be subjected to must be considered when estimating reusability. Insulator-based (electrodeless) microdevices can be considered if reusability and extended lifetime are desired.

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