INFLUENCE OF ELECTRICAL CONNECTION BETWEEN METAL ELECTRODES ON CONTIGUOUS SOLUTE-FREE ZONES

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Abstract: Earlier, we reported solute-free "exclusion zones" in aqueous media next to various metal surfaces. Here we explore the effect of connecting zinc, which ordinarily shows a large exclusion zone, to platinum, which ordinarily does not. We found the connecting the two metals diminished the exclusion zone next to zinc, while it increased the exclusion zone next to platinum. Disconnecting resulted in return to control values. These effects were largest when the metals were juxtaposed relatively closely, and became smaller with increasing separation. The underlying mechanisms are considered.
Keywords: zink, platinum, water, exclusion zone.

1. INTRODUCTION

The water-metal interface has attracted attention recently because of its relevance for hydrogen production and also for energy storage and conversion, e.g., in fuel cells. The importance of these phenomena has motivated a large number of experimental [1−3] and theoretical [4−8] surface-science studies as well as electrochemically oriented efforts [9−10]. These efforts have included studies of water structure at metal-electrode surfaces using techniques such as surface enhanced Raman spectroscopy [11−12], surface infrared spectroscopy [13], surface enhanced infrared spectroscopy [14] and X-ray diffraction [9,15]. However, the nature of the water structure at electrode-solution interface is still not fully understood.

In this study, we explore the metal-water interfacial region by examining the local disposition of colloidal particles and solutes. If the interfacial water exists in an ordered, liquid crystalline state, then many solutes should be excluded [16−18]. In previous studies we confirmed the presence of extensive solute-free zones in water adjacent to various hydrophilic surfaces [19−26]. Termed "exclusion zones" or EZs, these solute-free zones have more recently been found also to exist next to various metal surfaces [26]. Among those metals, zinc showed the widest EZ (~200μm) as well as the largest fractional surface coverage. Other reactive metals showed relatively smaller zones with less coverage.

Also observed in the exclusion zone next to those reactive metals were positive electrical potentials, as confirmed by direct electrical measurements. That positive charge was accompanied by negative charge in the region beyond the EZ, the latter inferred from high pH values. Thus, the reactive metals induced a separation of charge in the adjacent water. On the contrary, noble metals such as platinum and gold did not generally show obvious EZs or charge separation, possibly because of the absence of any surface chemical reactions. The apparent absence of chemical reactions may be the reason why those metals are referred to as noble. Similar to our results, Schnur [4,27] proposed that the water bilayer structure on noble metals was unstable at room temperature, whereas on more strongly interacting metal surfaces some ordering persists. Although the width of water layers suggested in that study are modest relative to what we found, the basic idea was similar: that the water is more ordered adjacent to reactive metals than adjacent to noble metals.

In this work, we study the water behavior near platinum and gold surfaces, exploring how the behavior changes during electrolytic processes. From a previous study [26], zinc electrodes can form EZs of considerable size, but platinum and gold cannot. Here zinc and platinum were used in combination. By connecting the two metals, we found that the EZ built reversibly next to the platinum while diminishing next to the zinc. Thus some interaction was apparent between the metal-water interfaces.

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2. MATERIALS AND METHODS

Sample preparation. The metals used in these experiments included the following: zinc (0.25 mm thick, Sigma-Aldrich); platinum (0.125 mm thick, Sigma-Aldrich); and gold (0.125 mm thick, Sigma-Aldrich). Before use, the metal surfaces were cleaned. For zinc samples, surface oxidation layers were removed by sandpaper and rinsed with deionized water. For noble metals, platinum and gold, the surface was rinsed with deionized water. All experiments were carried out at 21-22°C.

Figure 1 shows the schematic of the experimental setup. The metal foils were cut to an "L" shape (25 × 10mm, with each leg 3 mm wide) with a hole (diameter = 2.5 mm) on the top. Platinum wire leads were wrapped around a nylon screw, so that electrical connection was made with the respective platinum or zinc metal. The two metals were placed vertically in a double-slotted chamber, 75 × 25 × 5 mm in length, width and height.

The water used in all experiments was obtained from a NANOpure Diamond ultrapure water system. The purity of water from this system is certified by a resistivity value up to 18.2 MΩ·cm, which exceeds ASTM, CAP, and NCCLS type-I water requirements. In addition, the deionized water was passed through a 0.2µm hollow fiber filter, ensuring bacteria- and particle-free water. The pH of the resulting water was between 5.5 and 6.5.

To measure the size of the exclusion zone, various microspheres were used, including: carboxylate (2.65% solid-latex, Polysciences Inc.), polystyrene (2.65% solid-latex, Polysciences Inc.), amino (2.66% solid-latex, Polysciences Inc.) and amidine (4.1% solid-latex, Invitrogen). All were 1 µm diameter. The volume fraction of the microsphere suspension was 1:400, microspheres to water. In experiments, the chamber was placed on a microscope stage, and 2 mL of the microsphere suspension was slowly pipetted into the chamber.

Figure 1. Schematic of the experimental setup for observing the EZ next to metals

Microscope Observation. A Zeiss Axiovert 35 microscope was used for all observations. A high-resolution, single chip, color digital camera (CFW-1310C), well suited for low-light color video microscopy, was used for capturing images. The chip has a pixel resolution of 1360 × 1024 and a dynamic range of 10 bits. The CCD sensor employs the widely used Bayer color-filter arrangement. All image processing was done by MacBiophotonics ImageJ software.

Current and Voltage Measurements. A Keithley 6512 programmable electrometer was used for current and voltage measurements. For voltage measurements, a reference electrode was placed some distance from the two metals in same chamber.

pH Measurements. A Riedel-de Haën Universal indicator (Sigma Aldrich) was used to visualize pH distribution between the two metals. To observe pH color changes, we used a clear plastic petri dish (60 mm x 15 mm) that contained a slotted polystyrene block in which the metal pieces were held vertical and parallel. Four slits in the polystyrene block were separated by 5mm from one another, and were used to provide different electrode separations. The dye indicator was diluted as per the manufacturer's recommendation and 10 mL was poured slowly into the petri dish. Local pH changes were recorded and imaged using the CCD camera.

3. RESULTS AND DISCUSSION

3. 1. Exclusion Zones Near Active and Noble Metals

From a previous study [26], exclusion zones were found adjacent to active metals but not noble metals. Figure 2 displays representative images of

the results obtained when reactive (zinc) and noble (platinum) metals were placed in a chamber with a colloidal microsphere solution. The results confirm previous observations.

Platinum is widely used as a reference electrode in electrochemical and biophysical studies because of its stability: i.e., the absence of redox reactions, high electrical conductivity, and relatively low thermal conductivity. What remains unknown is the nature of the interaction that occurs when a noble metal is connected to a reactive metal, and what influence water may have on that interaction.

3.2. Microscopic Observations of EZ with Active and Noble Metal Interconnection
3.2.1. Control Experiments

Control experiments were first carried out in situations in which electrodes remained unconnected. Zinc and platinum foils were placed in the chamber containing a polystyrene microsphere suspension

(Fig. 1). Electrode separation was 10 mm. Figure 4 shows that an EZ began forming almost immediately near the zinc electrode, reaching a stable size of approximately 250 μm in approximately 10 minutes. The large standard deviations may arise from the non-uniformity of surface oxidation levels between runs. In this same chamber, no EZ was present next to the platinum electrode, as also shown visually in Figure 2.

3.2.2. Observations of the EZ near Zinc and Platinum Following Electrical Connection

Following periods of control, we connected the platinum and zinc foils together with a platinum wire. The connection was initiated 20 minutes following the injection of the polystyrene suspension. By this time the system had easily equilibrated, and the EZ near the zinc remained at a steady size.
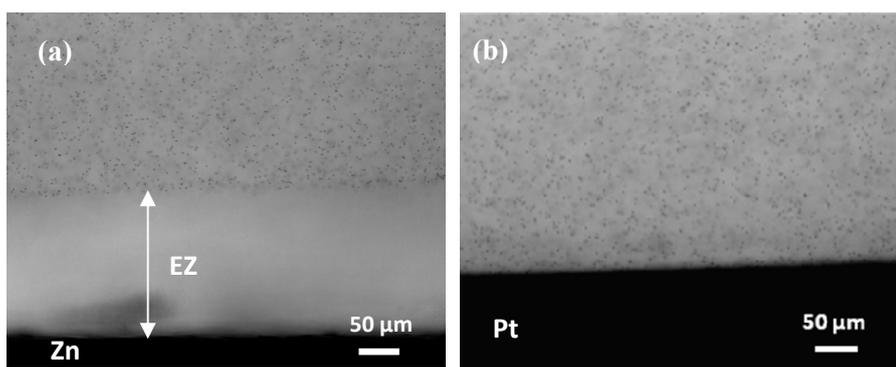
Figure 2. (a) Representative image of an EZ formed next to zinc in a polystyrene microsphere suspension; (b) Platinum, under similar conditions, shows no EZ.
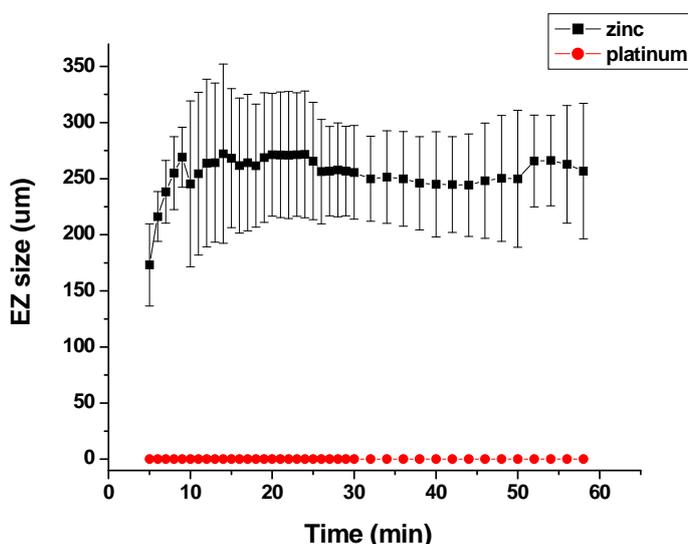
Figure 3.Exclusion zone buildup next to zinc and platinum, in aqueous polystyrene microsphere suspension. No electrical connection between electrodes.
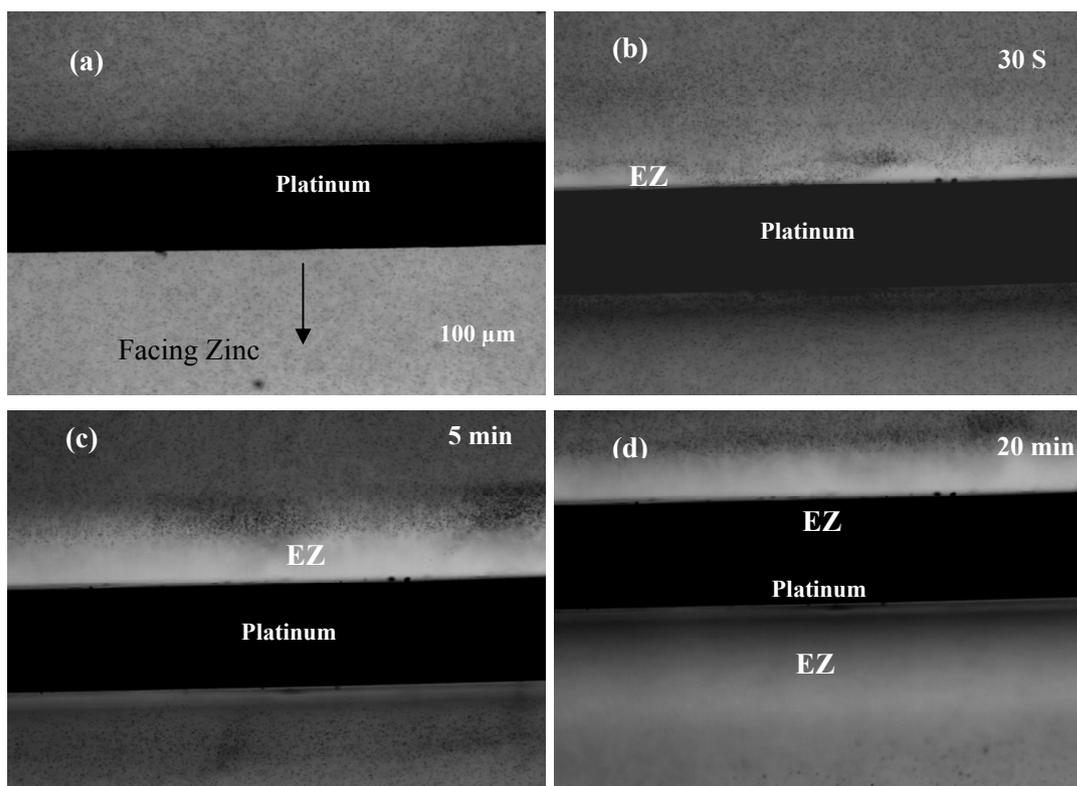
Figure 4. (a) Pre-connection: no EZ next to platinum. Following connection (b, c, and d), an EZ began growing next to platinum, as shown at various times.
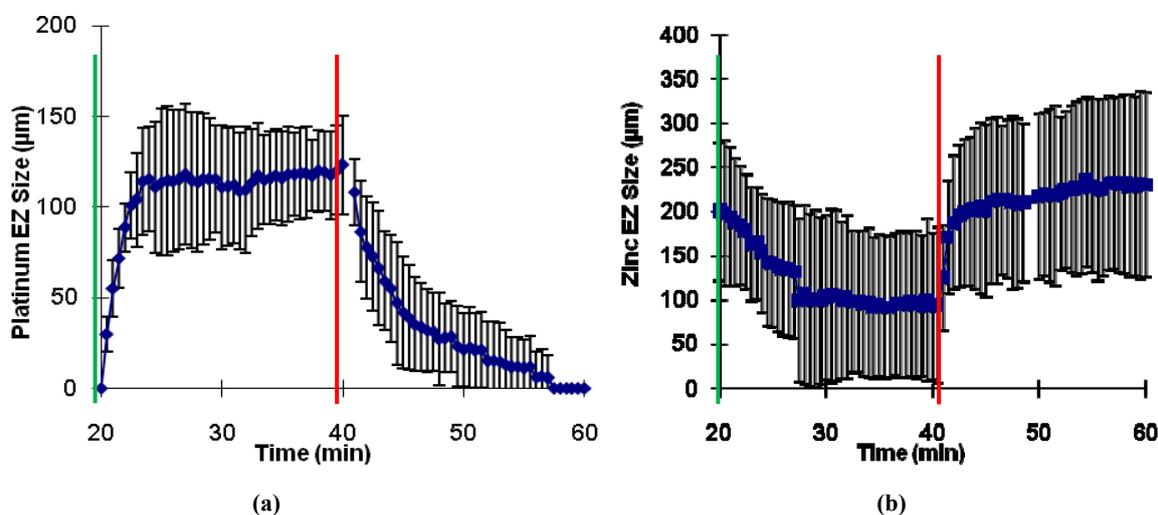
Figure 5. Exclusion zone size following electrical connection between zinc and platinum. Green vertical line denotes time of connection, red line time of disconnection. Polystyrene microsphere suspension.

As soon as the two metals were electrically connected, a near-platinum EZ manifested rapidly. The EZ expanded with time, as illustrated in figures 4(b), (c) and (d). During the same period, the EZ adjacent to the zinc surface decreased with time. Hence there was a reciprocal change of EZ size.Quantitative data are shown in Figure 5. The figure shows the formation and decay of the EZs near platinum and zinc on the sides facing one other. By five minutes following connection, the platinum EZ remained at a stable size *(a)*, whereas the zinc EZ continued to decrease somewhat, finally gaining stability after seven minutes *(b)*. After removing the connection, the platinum EZ decayed exponentially, reaching zero after about 17 minutes. The zinc EZ, by contrast, grew back to its original size after five

minutes, and continued to grow slowly thereafter to a slightly higher level.

On the opposite side of the platinum, facing away from the zinc, EZ size at the beginning was much larger than on the other side: 350 μm vs. 125 μm. Dynamics of buildup and decay were similar to the opposite side, except that following disconnection, the decay to zero took more time than on the opposite side.

3.2.3. Effect of Connection Start Time

To determine whether the absence of a pre-existing EZ near zinc made a difference on the platinum during connection, the two metals were connec-

ted at the time the suspension was injected into the chamber. In this scenario, an EZ near zinc was not able to stabilize before the charge transfer occurred between the two metals. As shown in figure 6, an EZ formed near platinum at the moment of connection, and reached maximum size of~180μm within five minutes. This maximum size was not sustained, but gradually decreased. When the connection was removed at 20 minutes, the EZ decayed back to zero within 10 minutes following. Comparing figure 6 to figure 5(a), it appears that the dynamics of EZ size near platinum during connection and disconnection are similar. Therefore, the growth and decay of EZ size do not depend very much on starting connection times.
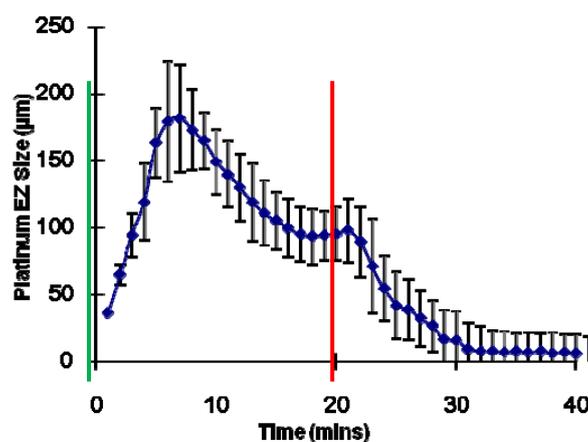
Figure 6. Exclusion zone size near platinum on the side facing to zinc, with connection immediately after injecting a polystyrene suspension (green line) and disconnection as indicated (red line).

3.2.4. Effect of Different Microsphere Types

To control for the possible effect of colloidal charge, several types of microspheres were tested and compared. The protocol used was: connection time at 20 minutes; duration 20 minutes; metals 10 mm apart. Figure 7 shows the platinum EZ size changes near platinum during connection with zinc. Three types of microsphere were used: carboxylate (negatively charged); amino (slightly negatively charged at pH>5; experimental pH=5.25); and amidine (positively charged at pH<8, experimental pH=5.68).

All microspheres except amidine showed similar trends: i.e., when the connection was initiated, the near platinum EZ increased in size, with time constants slightly different from those measured using polystyrene microspheres. When the connection was removed, EZ sizes decayed back to zero, again with slightly different time constants for carboxylate and aminomicrospheres. Amidine suspensions behaved differently in all respects: we found the even prior to connection, an EZ had

already formed next to platinum, and the connection-disconnection behavior was erratic. We estimate that the polystyrene microspheres may be the most reliable indicators of EZ size because of their near-zero charge.

3.2.5. Effect of Distance between Zinc and Platinum

We found that the distance between electrodes impacted the platinum EZ's formation and decay, as well as the current flowing between the two electrodes. In addition to the standard of 10 mm separation distance between electrodes, distances of 5 mm and 15 mm were tested.

For the separations of 5 mm and 15mm, the same phenomena appeared: the EZ formed near platinum surfaces when the connection with zinc was established, while it decayed to zero after the connection was removed. The difference between these three separations was the maximum size. The maximum sizes of the near-platinum EZs, respectively were: 5 mm: 200±30 μm, 10 mm:

120±20μm, and 15 mm: 80±10 μm. Hence size diminished with increasing separation.

The current flow between the electrodes was measured for all three separations. Similar to the sequence of EZ size, the peak current flowing through the connection between zinc and platinum was highest (~5.5 μA) for the 5mm separation; for the 10 mm and 15 mm separations, the current maxima were 2.0 μA and 1.8 μA respectively. We found also that the currents measured in the presence of polystyrene microspheres was similar to those measured with no microspheres at all, i.e., in pure distilled water. This finding reinforced the view that the polystyrene microspheres, because they lack charge are the most reliable indicators.

3.2.6. Metal Combinations

We substituted another noble metal, gold, for platinum to determine whether the characteristics were similar. The EZ next to gold grew during connection to approximately 75 μm, about one third the size of the platinum EZ, and it grew at a relatively slower rate. With disconnection, the EZ diminished

to zero in approximately 20 minutes. Hence, the results with gold were at least qualitatively similar to those of platinum.

4. VOLTAGE MEASUREMENTS BETWEEN PLATINUM AND ZINC

The voltage was measured between the wire connecting the two metals and a point in the water far from the electrodes. As shown in figure 7, all voltages increased with time and became stable after about 40 minutes. For pure water, the equilibrium (stable) voltage was approximately 200mV, which is similar to the electrical potential (220mV) previously measured near the zinc surface [26]. The order of voltage values (high to low) was amino, carboxylate, amidine, polystyrene and pure water. Again, the close values of pure water and pure water plus polystyrene microspheres indicates that these uncharged microspheres exert little influence on the results, while their presence permits EZs to be observed.
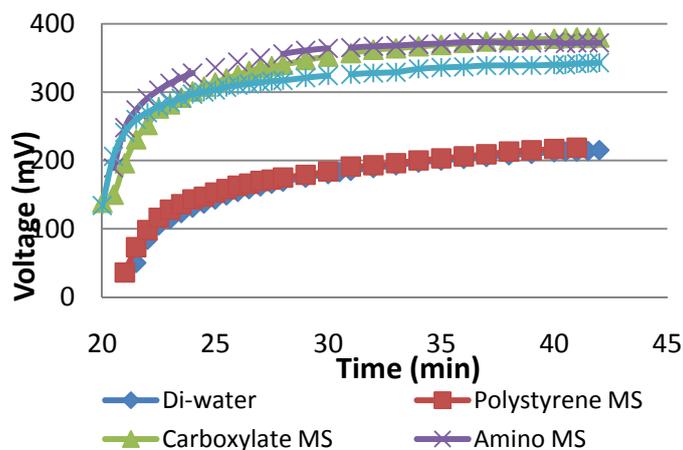
Figure 7. Voltage of zinc-platinum connection relative to a neutral point in the solution. Values given for pure water as well as different types of microspheres. (n=3).

5. pH INDICATOR OBSERVATIONS

Figure 8 shows the pH changes before, during and after connection. They are relatively low-resolution images, meant to show pH changes beyond the EZ. Initially, the red color indicates neutral pH throughout. However, the pH dye gradually changed from red (pH neutral) to yellow-green (basic) in the vicinity of the zinc. No change was observed near platinum. This result is similar to what was earlier found: [26] increasingly high pH in the region beyond the zinc EZ.

When the two metals were connected, the color next to platinum changed to yellow and green

as well. In the case of 5 mm and 10mm separation distances, the pH indicator changed to purple (very high pH) near platinum in the later times of connection. This purple color always appeared on the side facing the zinc. Meanwhile, when the separation distance was 15mm the range of color change near platinum was less distinct. Disconnection, on the other hand, resulted in progressive diminution of the extreme pH values. It appears from these observations that essentially, the pH changes that ordinarily occur beyond the zinc EZ transfer to the platinum EZ during connection.
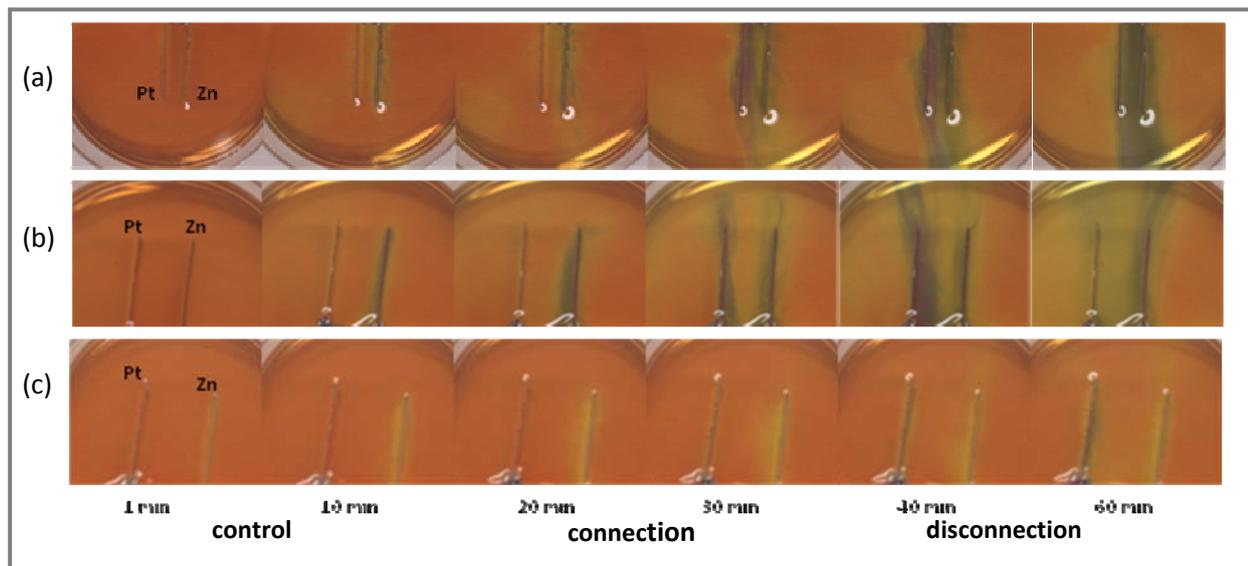
Figure 8. Time course of pH changes with different separations between zinc and platinum: (a) 5mm; (b) 10mm; (c) 15mm. Three situations: 0-20 minutes. control; 20-40 minutes, connection; and 40-60 minutes, disconnection.

6. CONCLUSIONS

The results imply a critical nature of charge in building exclusion zones. When immersed in water, zinc becomes charged as a result of the charged exclusion zones abutting its surface. Platinum ordinarily shows no such exclusion zone. However, when it is electrically connected to zinc so that charge can flow from one metal to the other, platinum does build an exclusion zone. The platinum EZ shows much the same characteristics as the one next to zinc. Thus, the flow of charge into or out of exclusion zones can easily regulate exclusion zone size, or indeed, whether an exclusion zone forms at all.

Remaining unclear is the mechanism underlying the distance effect. Distance between electrodes plays some role in the magnitude of charge separation (Fig. 8). A possible explanation may lie in the effect of the electric fields lying between electrodes, but any such effects will require further study.

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УТИЦАЈ ЕЛЕКТРИЧНЕ ВЕЗЕ ИЗМЕЂУ МЕТАЛНИХ ЕЛЕКТРОДА
НА ДОДИРНЕ ЗОНЕ БЕЗ ПРИСУСТВА РАСТВОРЕНИХ СУПСТАНЦИ

Сажетак: Раније смо обрађивали „зоне искључења“, одн. зоне без растворених супстанци у воденом медијуму поред различитих металних површина. Овдје истражујемо ефект повезивања цинка, код кога се обично јавља велика зона искључења, за платину, код које обично нема ове зоне. Установили смо да је повезивање два метала смањило зону искључења уз цинк, а повећало зону искључења уз платину. Након раздвајања поново су добијене контролне вриједности. Ови ефекти су били највећи када су метали стављани један поред другог на релативно малој раздаљини, а смањивали се при повећању раздвајања. Разматрали смо механизме који су у основи ових процеса.

Кључне ријечи: цинк, платина, вода, зона искључења.

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