Revisiting the Beating Mercury Heart Systems: Steps in the Voltage Figures Due to Nanocontacts

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We have revisited the problem of the beating mercury systems for acidic and basic medium. The results are analyzed in terms of electrochemical process and direct conduction of electrons between nanocontacts (contacts of few atoms size) formed by Fe and W with Hg in the acidic and basic medium, respectively. It is observed that, in some cases, the voltage(current) does not drop abruptly during the contact process (direct conduction), but in the steps that are related to the size of the nanocontacts. The phenomenon is similar to the one observed in the nanocontacts formed by metallic wires in which the conductance is quantized. Also, the analysis takes into account the completion electrochemical formation, of the film on the mercury ball in the acidic medium during the electrochemical process. The agreement between theory and experiment is very good when the nanocontacts conductance and completion of the film is added to previous existing theory.

I. Introduction

Recently, Costa-Krämer et al.[1] have shown that the current flowing through the nanocontacts formed when macroscopic contacts break apart is quantized, i.e., the conductance appears stepwise having units of quantum of conductance ($2e^2/h$) where e and h are the electron charge and Planck's constant, respectively. On the other hand, voltage oscillations in beating mercury heart systems have been well-known for many years.[2,3] Initially, they were often treated as just being good demonstrations for education in electrochemistry.[4,5] In the early 1970's it was recognized that they are among the novel kinds of phenomena which occur in nonequilibrium systems.[6,7] To understand the mechanism of the oscillations, J. Keizer et al.[2] presented a detailed analysis and gave a kinetic model for nonfilm oscillators (basic medium), which we have adopted, with some modification, to explain our new experimental phenomena, i.e., nanocontact formation and completion of the formation of electrochemical film in the acidic medium. The reason for these typical oscillating values is the change in the charge density on the mercury surface due to the electrochemical processes modeled by the Butler−Volmer equation and the direct conduction of electrons to the mercury drop. With this idea we can explain the common oscillatory shapes of the voltage between mercury and the tip in both basic and acidic solutions. We note that, in this model, only two extreme conditions about the direct conductance of electrons have been considered, the connection between the contact and noncontact zones was represented by a vertical line in voltage vs time values (see Figure 1), which implies that the contact they used have no resistance or it is negligible. However, it should be mentioned that the typical saw-tooth-shaped or rectangular-shaped plots were commonly recorded on a long time base usually more than 10 ms. If we shorten the time base to less than 1 ms, then sometimes we would get some not only interesting but also important experimental facts, for example, steps appeared in the voltage-drop during the contact. This

means that the vertical line is only a part of the story, and underneath it there must be another phenomenon happening.

Narrow constrictions in the contacts between two conductive materials can show a quantum effect.[1,8,9] The value of the conductance σ is quantized in such a way that the conductance of a nanocontact takes the value:

$$\sigma = (2e^2/h)n \qquad (1)$$

Substituting the relevant constants into eq 1 implies $\sigma = (n/12906.7) \ \Omega^{-1}$, where n is the number of quantum channels in the constriction of the contact.[9] The examination and study of these types of nanocontacts has been done by driving a scanning tunneling microscopy tip into a sample first and then pulling it out.[9] Furthermore, it has been reported that is also possible to achieve these types of nanocontacts at ordinary room conditions just by tapping the table top on which lay two ordinary metal wires connected to each other loosely.[1] This kind of nanowire has been also produced between metallic liquids such as mercury or tin and an ordinary metal wire.[10] By just inserting the wire into the metallic liquid by hand and then pulling it out, it is quite easy to obtain one step in the plot of the current between the two materials; of course, it is also possible to get more than one step. It has been confirmed that this step normally takes between 0.1 and 1 ms, or the time corresponding to a nanowire formation.

In the present paper, we will show that, to explain the steps appearing in the plot of the voltage drop during the contact in the oscillatory mercury heart systems, it is necessary to make some modifications to the model mentioned above[2] by introducing the change of the value of conductance due to nanocontacts forming. Also, the rectangular-shaped plot of the voltage occurring in the acidic medium is explained by the completion of the film formation resulting from the electrochemical process in the surface of the mercury drop; once this film is formed, the potential of the systems takes a constant value until the contact process starts again.

II. Experimental Procedures

Voltage−time curves were recorded on the LeCroy 9362 oscilloscope. We investigated in detail several typical oscillators including acidic, strong oxidants like K_2CrO_4 and H_2O_2 systems and also a basic system in NaOH. The detailed experimental

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a Acid Medium Voltage shape
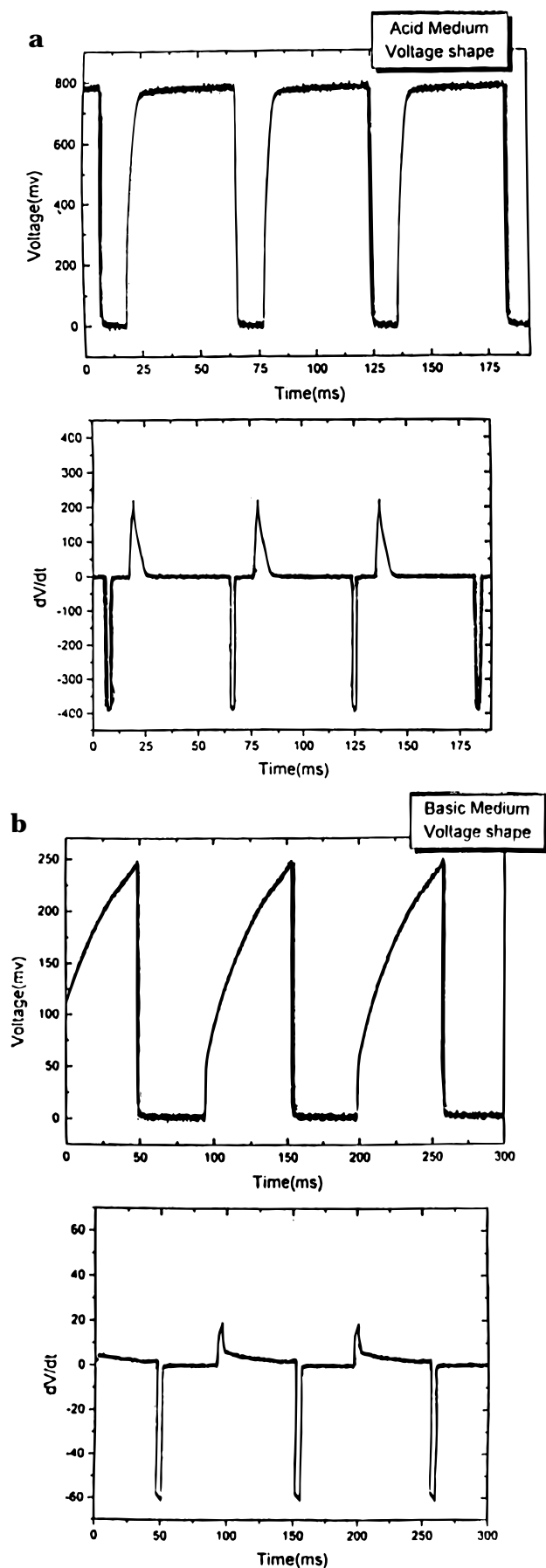

b Basic Medium Voltage shape

Figure 1. Typical voltage shape (upper plots of parts a and b) and derivative of such a voltage (current flowing) with the time (lower plots of parts a and b). (a) Plot is for the acidic medium (chromate system). The way up to the top voltage around 750 mV takes over 5 ms and the system maintains this situation for more than 40 ms (b) plot is for the basic medium. In this case the top value of the voltage is around 250 mV. It takes more than 50 ms to get to this situation from the contact position.

setup has been described elsewhere.[2] Reagent-grade chemicals were used without further purification. In the acidic system, a 6 M sulfuric acid and 0.2 M potassium chromate or 10% (v/v) hydrogen peroxide aqueous solutions were used, otherwise in the basic system, a 0.02 M sodium hydroxide was used with 0.98 M sodium chloride, thereby modifying the total ion strength to 1.00 M. In both systems, we use the common purpose mercury, cleaned several times by distilled water before use.

The general experimental procedure is as follows. Mercury was poured into a 125-mm watch glass to form a pool about 1 cm in diameter. Enough of the appropriate aqueous solution (which depended the investigated system) was added to cover the mercury completely. The tip was adjusted to the proper position to cause the mercury to oscillate, and as needed, we were able to adjust the distance between the tip and the mercury surface to obtain the desired total voltage. Note that some differences occur between the acidic and basic systems: in the former case, a corroding iron wire was directly used to trigger the oscillation from the edge of the mercury pool; however, a tungsten tip linked with the corroding aluminum was used to trigger the oscillation from the center of the mercury pool in the latter case.

III. Experimental Results

In acidic and basic systems, different shapes of the plots voltage oscillations were obtained. In the first case, the typical shape is always rectangular, and in the second case we always find a saw-tooth-shaped plot, which agrees very well with the results in ref 2, (see Figures 1a,b and for the voltage and current curves. The period of the oscillations is not always the same, even for the same system; it would primarily depend on the distance between the tip and the mercury drop. In the meanwhile, as we use the watch glass geometry, the inertia effect would also play a role to some extent. Anyway, it maintains an interval between 40 and 100 ms. The top voltage of the plot depends not only on the original position between the tip and the mercury drop but also on the concentrations of the active species in the solution. For the acidic system, we kept a top voltage value around 750 mV, and for the basic one, we kept the top voltage at about 250 mV.

The general way in which acidic systems go in and out of the top value of the voltage has been also studied in detail. Some differences appear between the chromate case and the peroxide one on the film formation systems. In those acidic cases, we know that the system takes over 5 ms for the chromate and about 2 ms for the peroxide system to arrive at the top voltage. For all systems, the top voltage is maintained for about 40 ms, but this time is also affected by the inertia.

Another characteristic time interval is that during which the voltage of the system goes to zero. Other authors[2] have described such a time as the moment when the tip touches the mercury and a short circuit is formed, and they give a value for that time between 10^{-6} and 10^{-7} s. We have studied that time in more detail for both the acidic and basic systems. For the basic systems, the process for voltage dropping from top down to near zero is always completed in about 10^{-5} seconds, and for the acid, it is about 10^{-6} seconds. In both systems, however, this time interval is really composed of two parts, a faster one smaller than 10^{-7} seconds (in this time interval the system decreases over 50% of the total voltage), and the rest of the time, that corresponds to values of microseconds or several decades of microseconds depending of the system, in which the system completes the fall to zero voltage (see Figure 2). We should mention again the inertia, as well as the film, in acidic systems or bubbles in the basic systems. Firstly, as we said before, we used the watch glass geometry, in which the
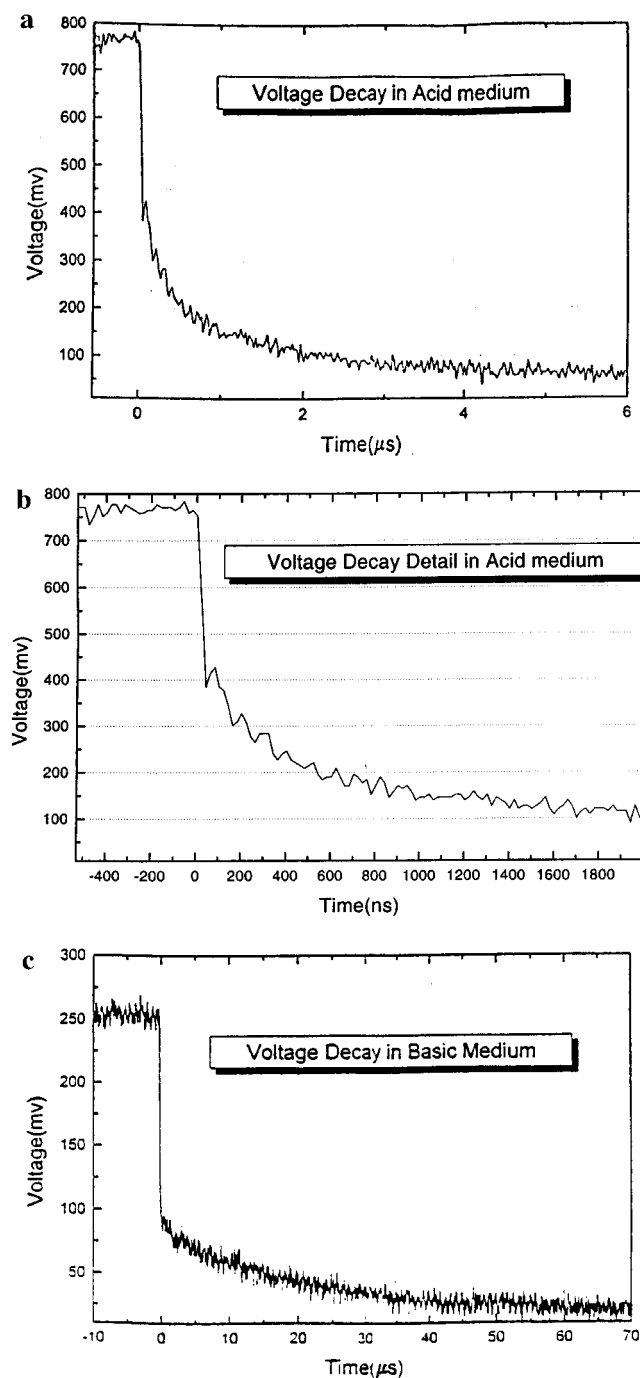
Figure 2. (a) Voltage decay in acidic systems. The process to get in contact takes about 4 μs, and part b presents details of the voltage decay in acidic systems. Within a time range of around 60 ns the voltage has dropped from 750 mV down to approximately 200 mV. (c) Voltage is shown decreasing in basic systems. In about 40 μs, the systems acquire the voltage corresponding to a short circuit.

mercury pool was not well confined that sometimes the mercury ball might roll on the watch glass surface due to inertia effect; secondly, in the acidic systems, when the tip touches the film, we observed that the film surrounding the mercury ball moves toward the tip and is destroyed there, but sometimes this process has not necessarily finished before the tip touches the bulk mercury again. While in the acidic systems, the gas bubbles containing hydrogen formed during oscillation must be desorbed and evolved out from the surfaces of both mercury and the iron tip before the tip can finally touch the bulk mercury. All of these factors can make those characteristic times mentioned above change in some uncontrollable way to different values, even on the order of milliseconds. We will try to improve this in our further investigation.
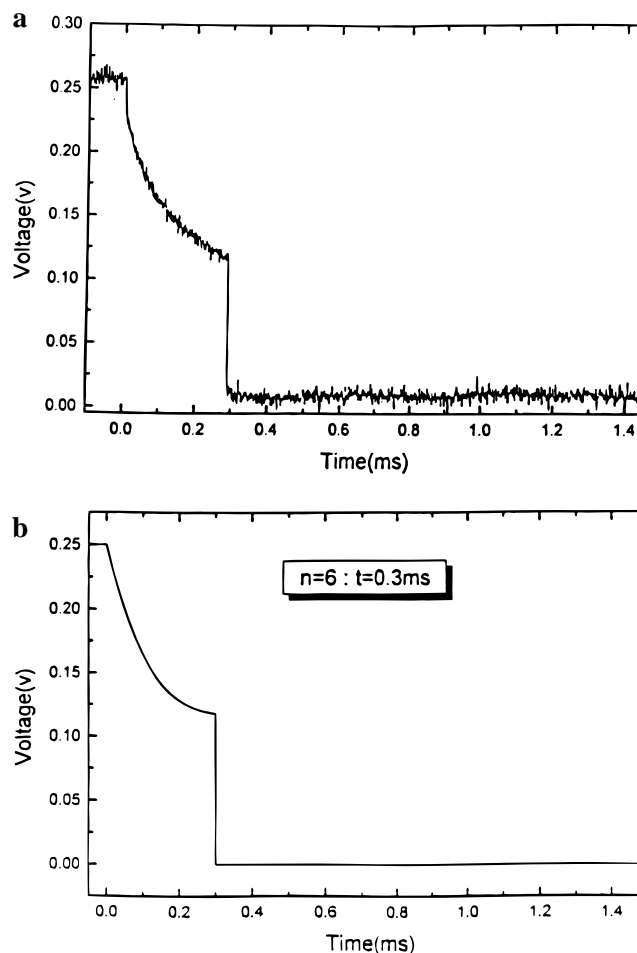

Figure 3. (a) Step in a voltage decay (in basic medium) lasting about 0.3 ms. The voltage at the end of the step is around 120 mV. (b) Computer simulation of part a is presented while considering that a quantum conductance of value $n = 6$ has been formed during 0.3 ms before the total contact takes place. The voltage at the end of the step is 118 mV.

These experimental facts agree very well with those described in ref 2. Nevertheless, we now focus on an other important observation, which very often occurs during the oscillation but which seems to have been neglected by other authors who had researched the mercury oscillation phenomenon. As we said before, the general situation is to find a sudden decrease in the voltage when the tip starts touching the mercury drop. However, we have noticed that for either acidic or basic systems, sometimes this decrease can take a longer time, and at the same time, between the top voltage and the so-called "short-circuit voltage", there appears a type of step which looks like an exponential decay being cut off suddenly. Although the number of the steps in the voltage vary, in most of cases we can only get one step. It is also very difficult, even impossible, to give a certain value about how fast is the decay to beginning the step, and also the end of the step seems to have no certain position in the voltage scale. (See Figures 3, 4, and 6 for basic and acidic medium, respectively).

IV. Analysis and Discussion

In the two cases (acidic or basic medium) the electrochemical reactions that take place during the oscillations are different from each other. We will discuss these cases separately.

Firstly, with the basic oscillator, when the tungsten tip touches the mercury the oxygen dissolved in the solution is reduced
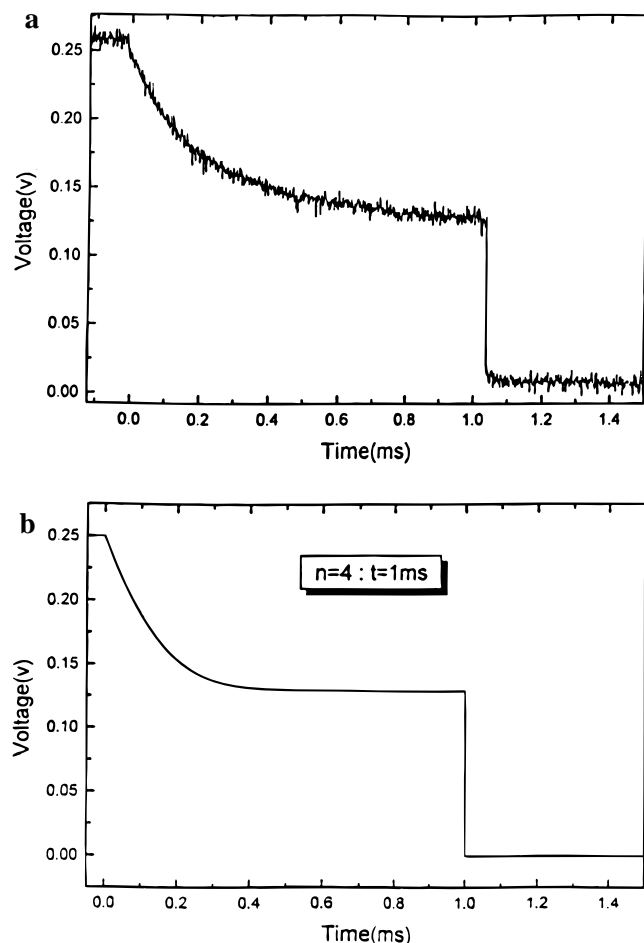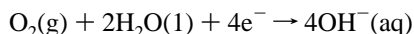
Figure 4. (a) Step in a basic medium lasting 1 ms. The voltage at the end of the step is around 129 mV. (b) Computer simulation of part a is presented while considering that a quantum conductance of value n = 4 has been formed during 1 ms before the total contact takes place. The voltage at the end of the step is 128 mV.

through the reaction:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

the source of electrons in this equation is given by the oxidation of the aluminum wire which is linked with the tungsten tip through the half-reactions,

$$Al(s) + 4\,OH^-(aq) \leftrightarrow Al(OH)_4{}^-(aq) + 3e^-$$

$$2H_2O(l) + 2e^- \leftrightarrow H_2(g) + 2OH^-(aq)$$
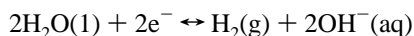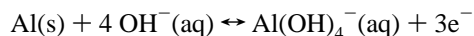
When the short circuit is created, the electrons given off by the aluminum go through the tungsten tip to the mercury surface and reduce the adsorbed oxygen there, which results in the change of the charge on mercury surface. The change of the charge on mercury surface changes the surface tension, which determines the mercury's shape: flat or round.

The voltage of the system depends on the electrochemical processes taking place on the two electrodes, in our cases the mercury drop and the tip or the corroding metal linking with the tip, and *also on the direct conduction of the electrons to the drop through the tip*. Taking a basic system oscillator, for an example and according to Model I in ref 2, we have the following differential equation for the voltage between the tip and mercury drop:

$$i = \mathrm{d}q/\mathrm{d}t = C\,\mathrm{d}v/\mathrm{d}t = i_0\exp(-v/v_0) - \sigma v \quad (2)$$
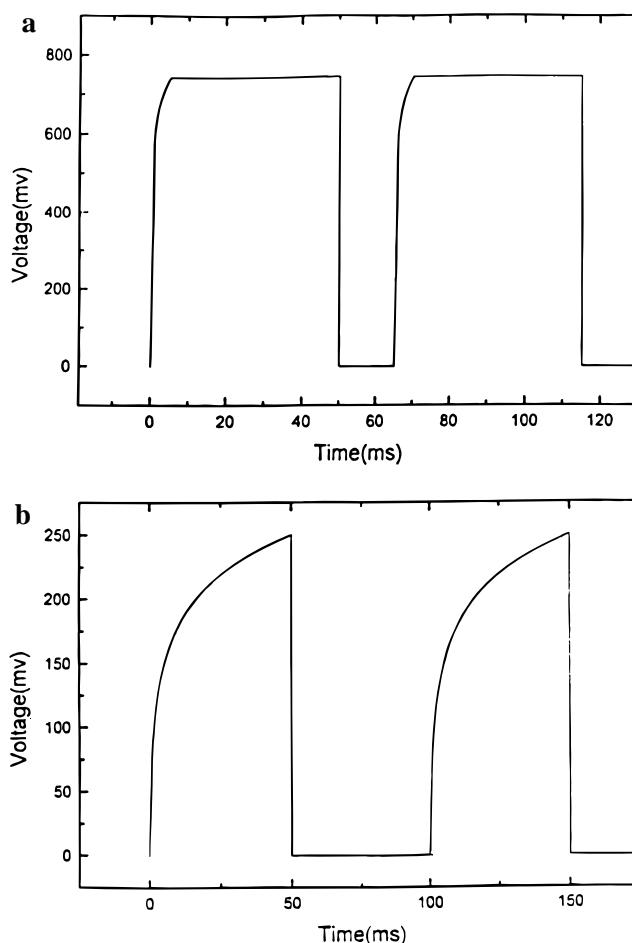

Figure 5. Computer simulations of the typical voltage decay: (a) in the acidic systems, in which 5 ms as the time for the voltage to get a value around 750 mV and 45 ms as the time until the system gets in contact again (the period considered is equal to 65 ms) are considered and (b), in the basic systems, in which 50 ms as the time for the voltage to get a value around 250 mV (the period considered is equal to 100 ms) is considered.

where i and q are the current and the charge of the system and C is the capacitance. The first term on the right comes from the electrochemical processes and is modeled by the typical Butler−Volmer form for low voltages, which in a first approach is a good approximation, and the second term represents the direct conduction of electrons, where σ is the conductance that, when the tip begins to touch the mercury surface, is finite but not as large as 20 Ω^{-1} (see ref 2) due to the small size of the contact (see ref 8 and references therein). As for the other parameters in the equation, i_0 corresponds to the cathodic current or exchange current, and such a current is proportional to the number of electrons that are involved in the electrochemical current, to the concentration of the active species, and to the standard rate constant k^0. This constant is in relation to the nonequilibrium of the transition of electrons in the electrochemical reaction and can take a wide range of values. For our calculations in the basic medium we take i_0 in the range from 7×10^{-3} to 7×10^{-4}A for a mercury surface area of about 1 cm^2. For the other parameter we take $v_0 = 0.045$ V (see ref 2). This parameter is in relation to an empirical constant called the Tafel constant (b) that is inversely proportional to the charge (or number of electrons) involved in the reaction n_e. For the basic system, $n_e = 4$, and for the acidic one, $n_e = 2$.

Now the typically shaped plots (*without any step*) can be explained in the following way:[2] when the tip gets away from the mercury the conductance can be considered as zero, so eq

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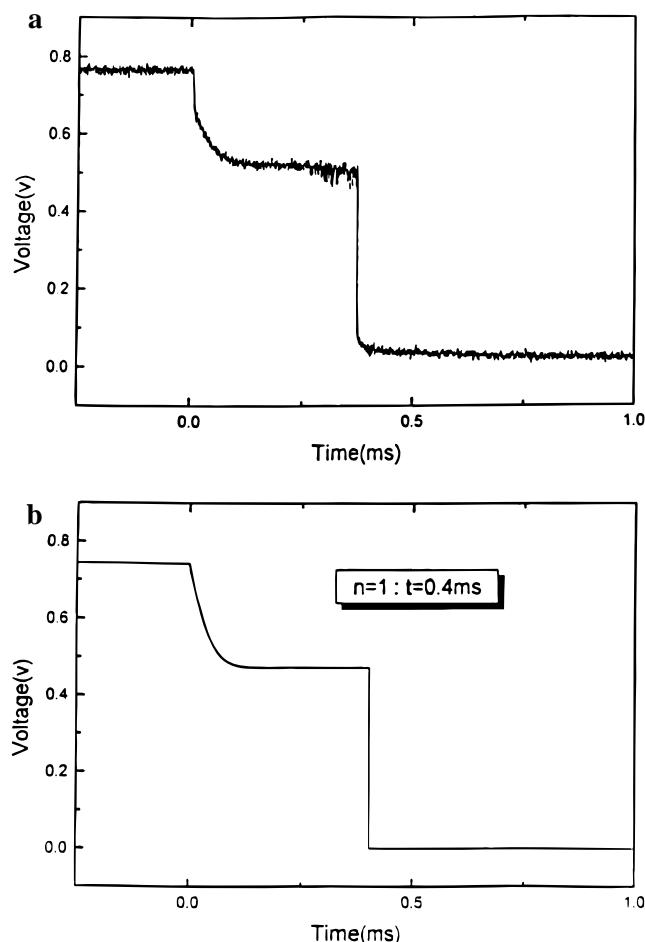
a

b

n=1 : t=0.4ms

Figure 6. (a) Step in acidic medium (chromate system) lasting 0.4 ms. The voltage at the end of the step is around 490 mV. (b) Computer simulation of part a is presented while considering that a quantum conductance of value $n = 1$ has been formed during 0.4 ms before the total contact takes place. The voltage at the end of the step is 473 mV.

2 takes the following form neglecting the second term:

$$C \, \mathrm{d}v/\mathrm{d}t = i_0 \exp(-v/v_0) \tag{3}$$

the solution to this differential equation is,

$$v(t) = v_0 \ln[(i_0 t/C v_0) + e^{v(t_0)/v_0}] \tag{4}$$

where $v(t_0)$ is the value of the potential at the time t_0 that corresponds to the moment when the tip and the mercury drop just get out of contact, in our case $v(t_0) = 0$. This is the behavior until the tip again touches the mercury surface. Then, the conductance takes a finite value about 20 Ω^{-1} when a short circuit is created and the voltage becomes almost 0 mV. With this behavior we get the typical saw-tooth-shaped plot for the basic system.
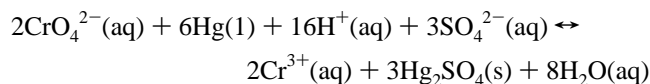
One possible way to explain the steps in the voltage with the mercury beating heart systems is to consider the nanowires[1,9] formed between the tip and the mercury surface. We introduce this idea to the second term in eq 2 instead of the two extreme situations used by J. Keizer et al., i.e., to substitute the quantum conductance in eq 1 into equation 2, giving the following equation:

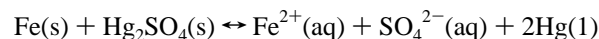$$C \, \mathrm{d}v/\mathrm{d}t = i_0 \exp(-v/v_0) - (2e^2/h)nv \tag{5}$$

For solving this equation, it is necessary to use some kind of numerical method, in our case we use the Runge−Kutta method, dividing the time interval of integration into 1000 steps. Here

the capacitance will play an important role. When the tip is in position, the capacitance takes a value of around 30 μF which was given by the Gouy−Chapman theory,[2] based on the double-layer theory. However, the regimes in which the nanowires may form, the tip is very closed to the surface, over 10 Å, and the electrochemical effect of the diffuse double layer over the capacitance can be neglected, leaving a capacitance per unit of area that is due to the compact double layer. The capacitance will be then proportional to the permitivity and inversely proportional to the distance, which gives us a value about 0.1 μF for a value of the mercury surface area of 1 cm^2. This is due to the Stern's modification. Several examples of the shapes obtained by computer simulation after modifying the Model I are showed in Figures 3b and 4b and may be compared with the experimental results (Figures 3a and 4a). The voltage falls down to the step in a soft way. As we can see, the effect of the nanowire is to introduce a voltage decay which becomes faster as n grows. Now we can easily understand why the time in which the systems get into the step is not a constant, precisely because it depends on the value of n. Once the total contact is formed, the voltage falls down to zero again. The voltage at the end of the step tends to a single value for each nanocontact formed, but if the time during which this nanocontact takes place is not long enough, the voltage at the end of the step is going to be different from the one we should get for a longer time interval. Therefore, each value of the nanoconductance implies different values of the voltage at the end of the step, depending on the nanocontact formation time, and we can understand why the end of the step seems to have no certain position in the voltage scale, that is, why the values of the voltage steps is not a group of constant values (one value for each n). Now all of the computer simulations in the figures agree well with the experimental results. A plot of several steps can be also used to explain a case in which a nanowire has gone through different values of the nanoconductance; this situation is not very normal for the case of liquid metals, but in our investigations we have noticed several examples of these types of nanocontacts.[10]

The results and analysis presented above are based on the nonfilm formation oscillators, i.e., the basic systems. But in the nearly same way, we can also explain the phenomenon for the acid systems, provided we have a correct choice of the electrochemical parameters. With the acidic oscillators, the principal difference from the above case is that the mercury plays a role on the electrochemical procedure, and there is a film formed on the mercury drop surface. We have investigated two acidic oscillators with different strong oxidizing agents: chromate and peroxide. In the first case the reactions for film formation and destruction are

$$2CrO_4^{2-}(aq) + 6Hg(l) + 16H^+(aq) + 3SO_4^{2-}(aq) \leftrightarrow$$
$$2Cr^{3+}(aq) + 3Hg_2SO_4(s) + 8H_2O(aq)$$

and

$$Fe(s) + Hg_2SO_4(s) \leftrightarrow Fe^{2+}(aq) + SO_4^{2-}(aq) + 2Hg(l)$$

respectively. These two processes cause the charge on the mercury drop to change and result in the mercury beating. For the peroxide system, only the reaction for creating the film is different from that one above:

$$2Hg(l) + H_2O_2(aq) + 2H^+(aq) + SO_4^{2-}(aq) \leftrightarrow$$
$$Hg_2SO_4(s) + 2H_2O(aq)$$
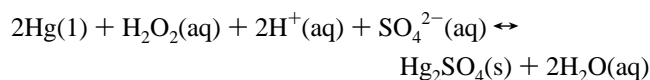
We note that the principal difference between the two cases is the creation of the film around the mercury drop in the acidic

medium. Once the tip gets away from the mercury surface, the electrochemical current starts to flow until the film is created, then the current becomes almost zero and there is no change in the potential of the system. Just when the tip starts to destroy the film and touches the mercury drop again, the current starts to flow to obtain a voltage that is almost zero. This fact is illustrated in Figure 1a, there we also show the curve of dv/dt vs the time which can be viewed as a qualitative measurement of the change in the current of the system; notice that the peaks with negative values represent the current flowing during the contact process, and the ones with positive values correspond to the current of the film formation process, and the values of the derivative equal to zero correspond to the cases in which the tip is inside the mercury or the film has been formed. For comparison, the same study is presented in Figure 1b for the basic system. In this case there is no film formation, and consequently once the tip does not touch the drop, the reduction of the O_2 on the surface of the drop results in a electrochemical current which results in positive peaks in the dv/dt vs time curve; this process will continue until the wire touches the surface of the mercury and releases the charges on the mercury surface, which are again represented as the negative peaks in the dv/dt vs time figure. There is only one situation for the system to have a current equal to zero, that is when the tip is inside the drop. Obviously, the results for these two different systems are different from each other.

On the basis of the discussion above, we can explain the typical square-shaped plot of the acidic system using the same model for describing the basic system. In the situation of nonfilm formation, the cathodic term $i_0 \exp(-v/v_0)$ is always equal to a nonzero value when the tip is away from the mercury surface. In the acidic systems, however, we know that the cathodic current i_0 must take a value equal to zero once the film has been formed because in this moment no electrochemical current is going through, and considering that the film is in fact a insulator,[2] the conductance maintains a value near to zero and then the Butler–Volmer eq 5 turns to be

$$dv/dt \approx 0 \tag{6}$$

for (tf $< t <$ tc) where tf is the time when the film has been created and tc is the time when the contact starts again. Equation 6 means v $\approx$ const, and this constant corresponds to the value of the voltage when the film has been completely created. Generally, this process will last about 45 ms until the tip touches the mercury surface again. Of course, the system takes just about 5 ms to reach the top value of the voltage, so the cathodic current must be larger than that in the basic case. The time intervals and values of dv/dt in Figure 1a,b are qualitative, but they clearly show how more quickly the potential for acidic system changes with time than that for the basic case; such a change is proportional to the cathodic current and inversely proportional to the capacitance so we can take i_0 in the range from 7×10^{-2} to 7×10^{-3} A, $C = 1 \mu$F, for a mercury surface area of about 1 cm^2 (higher cathodic current and smaller

capacitance that in the basic case). Also v_0 must be changed, the main reason is that this parameter is related directly with the Tafel b value that is inversely proportional to the charge involved in the cathode reaction process which is one half of that from the basic medium. We take then $v_0 = 0.09$ V for the acidic case. With these values of the parameters we obtain Figure 5a as a simulation of the typical voltage shape for the film formation systems, and Figure 5a may be compared to Figure 5b for the simulating result of the nonfilm systems.

Now we will discuss the steps in acidic systems. A Butler–Volmer form with a cathodic term and a value of the conductance due to nanowires formed can be used. Again, the capacitance, near the contact zone, can be considered to be under the effect of the Stern's modification, but considering that the presence of the film that is starting to be destroyed, which is in fact an insulator, can change the value of the permitivity to a smaller one, it may be reasonable to suppose $C = 10^{-8}$ F for the area of 1 cm^2, (10 times smaller than in the basic case). Figure 6a gives an example for experimentally observing the step in the acidic medium, and Figure 6b is the result of the computer simulation. Notice that main features are described with the modified model based on the nanowires formed on the surface of the mercury drop.

In conclusion we have shown that the voltage curves in the mercury beating heart systems can be better understood if the size of the nanocontact formed in the direct electron transfer mechanism is included. Also, for the acidic medium systems, we should consider the completion of the film on the mercury ball to explain the flat plateaus formed in the voltage curves. The agreement between experiment and the theory presented consolidates these ideas.

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