

Quantum Contact by Colliding 2D Fractal

S. Nakabayashi,^{*,†} H. Sakaguchi,[‡] R. Baba,[§] and E. Fukushima[†]

*Department of Chemistry, Faculty of Science, Saitama University,
Saitama, 338-8570, Japan, Research Institute of Electronics, Shizuoka University,
Hamamatsu, 432-8011, Japan, and Department of Marine System Engineering,
Tokyo University of Mercantile Marine, Etchu-jima, Tokyo, 135-8533, Japan*

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ABSTRACT

The quantum contact through which the electronic conductance is quantized by $2e^2/h$ was chemically formed in a beaker. This preparation method needed only conventional tools in a common laboratory. Quasi-two-dimensional zinc fractal was used as an electrode, which was electrochemically synthesized at an immiscible interface between water and 4-methyl-2-pentanone. The electronic conductance through the colliding atomic bridge between the zinc fractal and a copper ring electrode surrounding this 2D fractal was quantized at room temperature.

We are attempting to synthesize a specific structure in a beaker that can demonstrate a quantum electronic function. As the artificial structures become smaller than the size of the de Broglie wavelength of electrons (approximately a few angstroms), most of the quantum mechanical function becomes substantial.¹ Two opposite commonly used routes to the nanostructure are based on the concepts of building up the components and dividing down the body. From the viewpoint of chemists, the former route looks much more attractive because a lot of skills aiming at building up of atoms have been accumulated in chemistry.

In this article, we show that an electrochemical synthesis has succeeded to construct the nanostructure, which enables us to regulate the electron transport in a quantum mechanical manner.

The essential structure for the quantum electron transport is an atomic bridge between two metallic bulk bodies.^{2,3} Different procedures to form such structures have been reported; for example, a scanning tip manipulation using an STM unit aiming to form a gold nanowire between the gold substrate and the tip.^{4–6} Another example is a mechanical microfabrication of an atomic bridge by the use of a controllable break junction (MCB).^{7–9} Although these two techniques are the most reliable and reproducible ways to build up the nanoatomic bridge between two metallic bodies, much simpler and convenient procedure is expected to be developed because both STM and MCB techniques require special instrumentation and skills. The chemical method

based on electrochemical deposition and etching is one of the most promising counterparts to synthesize such structure.^{10–13} The most critical advantage of the electrochemical process is its controllability.^{11–13} Tao^{10–11,13} and Marcus¹² showed that by using proper feedback technique, the structure of the atomic bridge could be maintained over 1000–10000 s. This long-term stability of the structure made it possible to study the electron scattering effect by adsorption of some organic molecules on the bridge.¹¹ Although the electrochemical method has been well developed, it still needs a specific technique such as lithographic or STM methods. In this article, we will show that by using items common to usual laboratories the quantum contact can be formed.

At the two immiscible liquid interfaces, the molecular orientation of the solvent differs from that in the bulk solution.^{14–16} In the case of the nitrobenzene and water interface, especially when an electrochemical potential was applied, we have shown that nitrobenzene molecules appeared to have a liquid-crystal-like ordering at the interface and thus induced the polarization anisotropy in the refractive index at the interface.¹⁴ Nitrobenzene was suitable for this optical measurement because it has a large Kerr constant. The immiscible interface gives us an exotic reaction field. The electrochemical metal deposition at the interface has a special mode, which leads to the localization of the metal deposition mostly at the interface but not into the bulk solution.^{17–20} Then, the quasi-two-dimensional deposit could be formed at the interface, which was historically called the metal-leaf.²⁰

The schematic representation of the experimental setup for synthesizing the zinc metal-leaf and also for measuring the quantum electron transport is shown in Figure 1. We

* To whom correspondence should be addressed. E-mail; Sei@chem.saitama-u.ac.jp.

[†] Saitama University.

[‡] Shizuoka University.

[§] Tokyo University of Mercantile Marine.

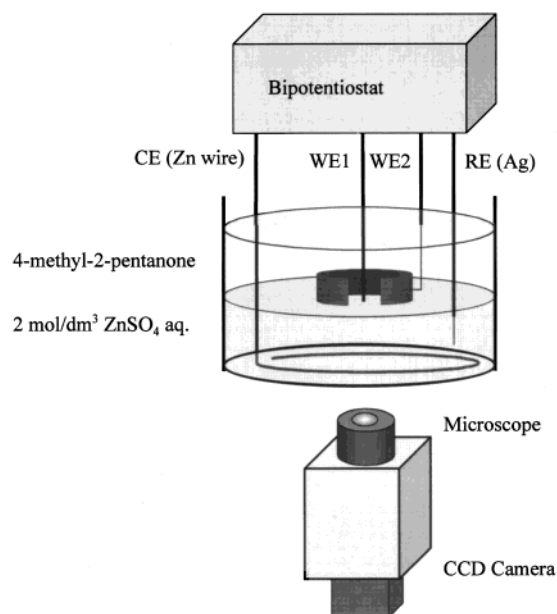


Figure 1. Schematic representation of the experimental setup for the synthesis of zinc metal-leaf around carbon electrode (WE1, -5.0V) at the immiscible liquid–liquid interface. The quantum electron transport was measured with the same setup by observing the time profile in the current across the copper electrode (WE2, -0.122V), where the current is due to the electron transport from the copper electrode to the Zn fractal electrode. CE and RE in the figure represent the counter electrode and the reference electrode, respectively.

used the liquid–liquid interface between 4-methyl-2-pentanone and 2 mol/dm^3 aqueous solution of zinc sulfate. We avoided nitrobenzene because it is more reactive electrochemically than 4-methyl-2-pentanone. To synthesize Zn metal-leaf, a carbon electrode (WE1) whose diameter was 0.3 mm was placed with its tip end touching right at the interface. The counter (Zn) and the quasi-reference (Ag) electrodes were placed in the aqueous solution. The morphology of the Zn metal-leaf was examined as a function of the applied potential. The current for the reduction of the zinc ions and the shape of the deposit was varied by the potential. The current also changed as the area of the Zn deposit increased. To reduce the effect of the variation of the electrode area, the current was measured immediately after the potential step was applied. The electrode potential was stepped from the rest-potential (-0.122V vs Ag) to the potential of a given value and the height of the current response which obtained 1 ms after this step was plotted as a function of the final potential. As it is shown in Figure 2, within the small overpotential region, the current increased exponentially as the potential applied. However, the saturation in the current was observed in the potential region far from equilibrium. Simultaneously with this change in the current as the overpotential increased, the shape of the deposited Zn leaf was changed from disk to fractal. The exponential increase in the current corresponds to so-called Tafel relation,²¹ which shows that the rate of the electrode reaction, i.e., the deposition of zinc, is limited by the electrochemical electron transfer. However, the saturation of the current at higher overpotential range suggests that the

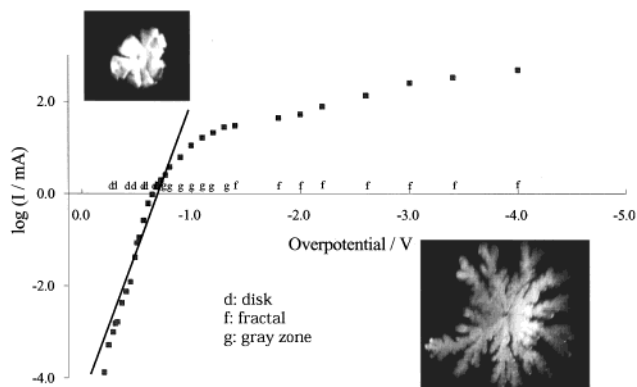


Figure 2. Logarithm of the current as a function of the final potential. ‘d’, ‘f’, and ‘g’ along the potential axis denote the pattern of the deposit and the pictures at the upper left and lower right are typical shapes of the deposit, disk (d) and fractal (f), respectively. In the region of (g), the obtained pattern was inconsistent and not fixed.

reaction speed is limited by the diffusion of the zinc ion.²¹ In the region far from the equilibrium, for example -5.0V , the fractal dimension (D) of the deposit was identical with the value of D for the diffusion-limited aggregate (DLA): $D \approx 1.6-1.7$.²⁰ This shows that the deposition of a zinc atom proceeds at every collision between the zinc ion and the deposit. At the same time, this implies that the diffusion of the zinc ion at the interface is much quicker than that in the bulk solution, which is probably due to the specific molecular configuration at the liquid–liquid interface.

The morphology of the deposit under the potential region far from the equilibrium can be considered in terms of quasi-two-dimensional DLA, though the deposited leaf certainly grew thicker very slowly into the bulk solution. The reaction front at the top of the fractal finger must consist of uppermost atomic layer localized at the interface. Even though the topmost surface atomic layer of metal zinc is oxidized easily in the air, these atoms at the top of the fractal are free from oxidation due to controlled electrochemical potential and to the sealing from the air.

By using a bipotentiostat (Nikko-keisoku DPGS-1), the electrochemical potentials of the zinc fractal electrode (WE1) and the curved copper plate electrode (4.5 mm in diameter, WE2) were controlled with respect to the common reference electrode. The potential of the zinc electrode was set at -5.0V and that of the copper electrode was kept at the equilibrium potential where no electrochemical reaction could proceed on it. A schematic representation of the collision between Zn fractal and the surrounding copper electrode is shown in Scheme 1. The time evolution of the current through the copper electrode was measured simultaneously with the observation of the growth of the zinc fractal through a CCD camera. As shown in Figure 3, just before the collision, a trace of the current (ca. 0.1 mA) was flowing across the copper electrode. This current might be produced by the change in the concentration of zinc ion near the copper electrode surface, which was induced by the growth of the zinc fractal finger approaching to the copper electrode. Just after the collision between the zinc fractal and the surround-

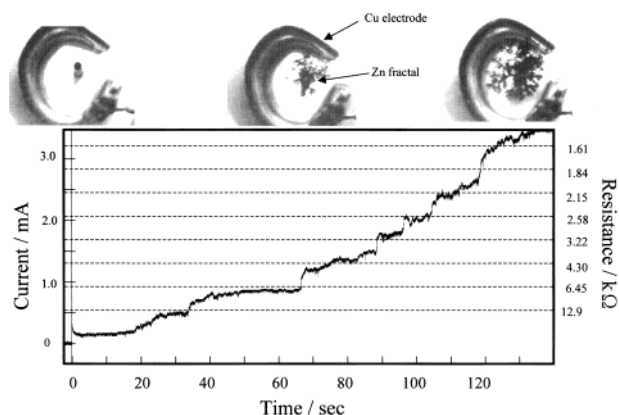
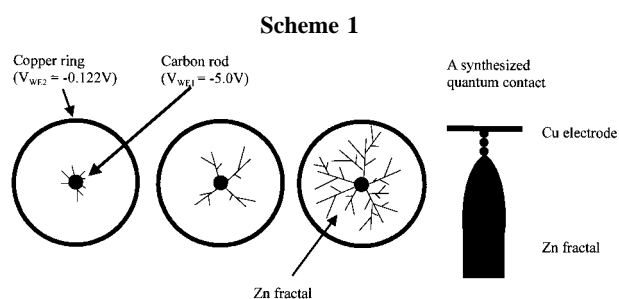


Figure 3. Time evolution of the current observed through the copper electrode. The potentials of the zinc and the copper electrodes were set at -5.0 V and at the equilibrium (-0.122 V) to the common quasi-reference electrode, respectively. The pictures above are the growth of the zinc fractal electrode observed by a CCD camera. The dotted lines indicate the current steps corresponding to $\Delta V/12.9$ k Ω .



ing copper ring, the observed current was increased. The increase in the current was not monotonic but a staircase-like profile was obtained.

According to the theory of the electron transport through an atomic bridge, the quantized resistance for the current staircase must be $h/2e^2 = 12.9$ k Ω .¹⁻³ As the guide for eye, the current response was sectionalized with dotted lines in the figure indicating the steps corresponding to $\Delta V/12.9$ k Ω , where ΔV is the potential difference between the fractal zinc and the copper electrodes, i.e., $5.0 - 0.122 = 4.88$ V. Each height of the observed staircase was not exactly the same but fairly close each other to the value of 4.88 V/ 12.9 k $\Omega = 378$ μ A. The observed behavior suggested that the resistance at the contacts between zinc fractal and the surrounding copper electrode decreased stepwisely by 12.9 k Ω/N , where N was the number of the quantum contacts formed.

Because the zinc fractal can be electrochemically dissolved by switching the polarization to the anodic direction, it is very simple to repeat this colliding experiment of the fractal leaf against the copper electrode. These repeated cycles of successive deposition and dissolution of the zinc fractal can be simply achieved by controlling the electrode potential. Every contact formed between the top of the zinc fractal and the surrounding copper is fresh whenever the current staircase is measured, because the zinc atom located at the end of the fractal finger has been just reduced from zinc ion. After 124 cycles, the number of the events that give

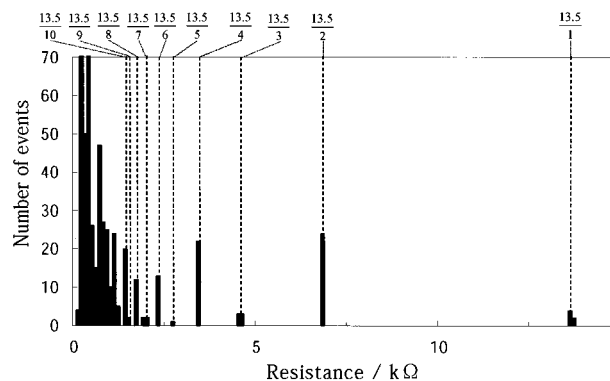


Figure 4. Histogram of the number of the events when each different resistance value was obtained. The harmonics ($13.5/N$ k Ω) were shown above.

different resistance were counted as a function of the resistance. The obtained histogram is shown in Figure 4. The fundamental resistance for the unit staircase in the current was not 12.9 k Ω but 13.5 k Ω . The histogram had peaks at 13.5 k Ω/N ($N = 1, 2, 3, \dots$). At the initial increase in the current, when only one finger of the fractal contacted with the copper ring, the single height staircase was observed. If the two fingers contact simultaneously, the initial height of the staircase would be the double. As the number of the contacts increases, the current jumps up accordingly whenever a new contact is formed. This is the most probable reason for obtaining the harmonics in the resistance like 13.5 k Ω/N . In a couple of minutes when a lot of contacts are formed, this harmonic relation disappeared because the intervals between the quantized resistances decrease quickly and finally the bulk resistance appeared instead of the quantum resistance. Interestingly, the occurrence in the histogram corresponding to the even numbers of the contacts (i.e. $13.5/2$, $13.5/4$ k Ω , ...) are always more frequent than those corresponding to the neighboring odd numbers. So far, the similar structure in the histogram for the quantized resistance has not been reported in STM and MCB experiments. In almost all of the cases, a monotonic decrease in the peak height toward the higher harmonics has been reported.^{5,10} At this stage, we suppose this even/odd regulation in the histogram might be influenced by the DLA structure of the Zn fractal rather than by the electronic structure of Zn.

The reason for the discrepancy in the resistance between 12.9 and 13.5 k Ω is not so clear at this stage. But, in considering that the discrepancy is frequently observed in d-metals and that the normal resistance of 12.9 k Ω is generally observed in sp-metal,^{5,7,8} this difference is certainly affected by the electronic character of zinc atom.

This fractal method is also applicable to other metals and, further, to the study under controllable circumstances such as magnetic field.¹⁹ Moreover, this method is actually one of the most simple procedures by which to study the physics and the chemistry of quantum metal contact.

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