# Propulsion of Microobjects by Dynamic Bipolar Self-Regeneration

Gabriel Loget and Alexander Kuhn*

*Université de Bordeaux, IPB, UMR 5255, ENSCBP, 33607 Pessac, France*

Received August 24, 2010; E-mail: kuhn@enscbp.fr

**Abstract:** Dynamic bipolar self-regeneration is a new mechanism that allows controlled motion of metallic microobjects to be induced. This technique is based on the concept of bipolar electrochemistry, in which different redox reactions occur at the two extremities of a substrate under the influence of an external electric field. To create the motion of a metallic object, one end has to be the site of metal deposition and the other the site of metal dissolution. Propulsion of zinc macro- and microswimmers at speeds of up to 80 $\mu$m s$^{-1}$ has been achieved.

The need for micro- and nanodevices that could move spontaneously or in a controlled way in order to perform various tasks at a small scale is increasing within the general frame of nanotechnology. Nature offers some beautiful examples of biomotors, such as the flagellar bacterian motor, kynesin, and dynein, that can be used to create motion at the nanoscale,[1,2] and since the early 1990s this has triggered a growing interest in the design of artificial micro- and nanomotors with precise control of their motion.[3] Different approaches have been used in order to induce the motion of these swimmers. Applying an external field, which can be magnetic,[4,5] electric,[6,7] or also UV light,[8] is one way to generate motion. Another approach consists of injecting a fuel that generates the motion by self-electrophoresis[9] or bubble propulsion[10] mechanisms. By this technique, micro- and nanoparticles such as wires,[11,12] rolled-up membranes,[13] and spheres[14,15] can undergo propulsion when they are functionalized with some catalytically active metal, enzyme,[16,17] or enzyme mimic.[18] Here, we report a new approach for triggering particle motion at small scales that is based on the dynamic bipolar self-regeneration of metal particles.

Bipolar electrochemistry on microobjects was first described by Fleishmann et al.[19] This appealing approach relies on the fact that when a conducting object is placed in a strong electric field between two electrodes, a polarization that is proportional to the electric field and the characteristic dimensions of the object occurs. The arising potential bias between the two ends of the substrate is given by the equation

$$\Delta V_{\text{min}} = Ed \qquad (1)$$

where $E$ is the total external electric field and $d$ is the particle size. This potential difference can be used to drive localized redox reactions. The concept has recently found applications in the elaboration of Janus particles,[20,21] as the driving force in electrochemiluminescent reactions,[22] as the detection mode in capillary electrophoresis,[23] in patterning,[24,25] the creation of electrical contacts,[26] and membrane pore functionalization.[27]

In this communication, we demonstrate that bipolar electrochemistry can be used to propel macroscopic or microscopic metallic objects by a dynamic self-regeneration process. This original approach consists of the combination of material deposition at the negatively charged end of the object and simultaneous dissolution of the same material at the positively charged end, which leads to

linearly directed motion (Scheme 1) analogous to what has been reported for immobilized particles.[28]

**Scheme 1.** Dynamic Bipolar Self-Regeneration Principle
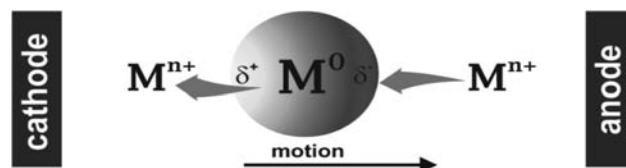


In order to carry out two redox reactions at opposite ends of the object, the potential between the opposite ends of the object, $\Delta V_{\text{min}}$, must to a first-order approximation be equal to the difference between the formal potentials of the two redox reactions. Equation 1 illustrates the need for very high electric field values (which can be on the order of 100 kV m$^{-1}$) in order to achieve reduction and oxidation using two different redox couples at opposite ends of a micro- or nanoparticle.[21] However, when the same fast redox couple at both ends of an object (Zn$^{II}$/Zn$^{0}$ in our case) is employed, lower electric field values are sufficient. In the present work, fields of up to only 7 kV m$^{-1}$ were needed.

As a proof of principle, first experiments were carried out at a macroscopic level. Zinc, which grows electrochemically with a dendritic morphology,[29] was electrodeposited at the extremity of a metallic wire inside a glass tube with an inner diameter of 0.6 mm filled with a 0.1 M zinc sulfate solution. When a deposit of a few millimeters length was obtained, the "swimmer" composed of zinc dendrites was disconnected from the zinc cathode by pulling the wire out of the capillary (Scheme 2). Finally, a potential difference of 125 V between two external electrodes separated by 10 cm was imposed, leading to an electric field with a value of 1.25 kV m$^{-1}$.

**Scheme 2.** Experimental Process: (A) Dendrite Growth; (B) Dendrite Detachment; (C) Dynamic Bipolar Self-Regeneration
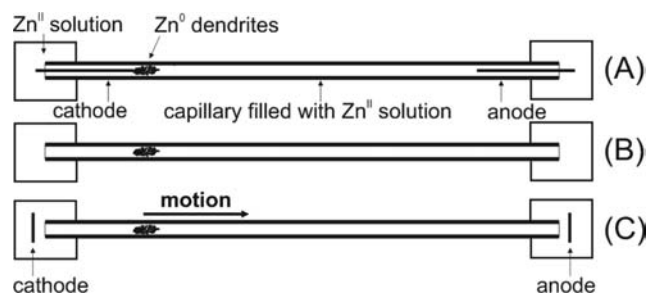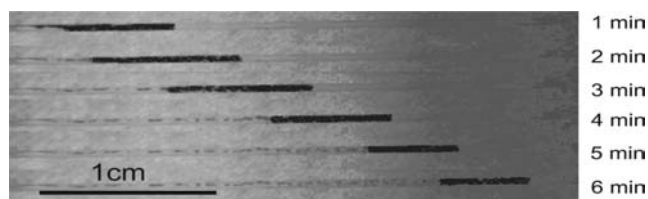


The following reactions occurred:

$$\text{Zn}^{\text{II}}(\text{l}) + 2\text{e}^- \rightarrow \text{Zn}^{0}(\text{s})$$
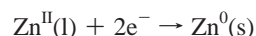
at the negatively charged end of the swimmer (right side) and

$$\text{Zn}^{0}(\text{s}) \rightarrow \text{Zn}^{\text{II}}(\text{l}) + 2\text{e}^-$$

**Figure 1.** Pictures of a zinc macroswimmer in a glass tube filled with a zinc sulfate solution under the influence of an external electrical field, recorded at various times (also see video 1 in the SI).

at the positively charged end (left side). As a consequence of these simultaneous reactions, the swimmer was directed from left to right at a speed of ~60 $\mu$m s$^{-1}$ [Figure 1 and video 1 in the Supporting Information (SI)]. Because of the nonhomogeneous density of the zinc object, its length varied during propulsion. Obviously, turning off the electric field stopped the motion. In these pictures, depending on the local pH conditions, the presence of a thin zinc oxide layer behind the moving object can be noticed, suggesting that the technique might be used for printing surfaces with a conducting or semiconducting "ink" that could be engineered by adjusting the swimmer composition.

This result encouraged us to perform analogous experiments at a microscopic scale. As in the previous experiments, a zinc dendrite was isolated in a capillary with an inner diameter of 100 $\mu$m filled with a zinc sulfate solution whose pH was adjusted by the addition of a small amount of acid in order to prevent zinc oxide formation during the experiment. Next, the swimmer was exposed to an external electric field of 7 kV m$^{-1}$, which propelled it at ~80 $\mu$m s$^{-1}$ (Figure 2 and video 2 in the SI).
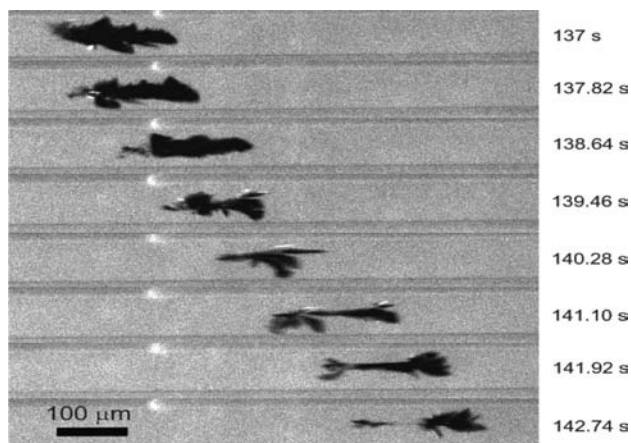


**Figure 2.** Optical micrographs of a zinc dendrite in a glass capillary filled with a zinc sulfate solution at pH ≈ 5 under the influence of an external electric field (also see video 2 in the SI).

The change of the swimmer morphology clearly shows that the motion was induced by the dynamic bipolar self-regeneration process and not by electrokinetic phenomena. Electroosmotic flow, which definitely existed in the capillary, was oriented in the opposite direction and therefore cannot explain the movement. We verified that inert carbon particles indeed moved in the direction of the electroosmotic flow. The dendrite could be propelled for several minutes over distances in the centimeter range. Obviously, it is possible to make this path longer by increasing the time of the experiment, and the speed can also be controlled by tuning the electric field value. The experiments shown here were carried out in one dimension because of the use of a capillary, but we also

performed similar experiments under open conditions (no capillary), in which the objects were more difficult to follow under the microscope.

In summary, we have developed a new approach to propel objects with a speed comparable to those reported in the literature for existing methods. The process can be generalized to other metals, as we have made similar observations using copper. We have shown that it is possible to induce motion at the macro- and the microscale, and it is straightforward to extend the same mechanism also to the nanoscale, although in that case imaging of the motion becomes more complicated. In the future, dynamic bipolar self-regeneration could be used, for example, for wireless localized deposition, making electrical contacts at the nanoscale, or surface patterning, as the process is very robust with respect to changes in experimental conditions.

**Supporting Information Available:** Two videos (AVI) showing the motions of (1) the zinc macroswimmer in a glass tube filled with a zinc sulfate solution and (2) the zinc dendrite in a capillary filled with a zinc sulfate solution with adjusted pH. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

(1) Goel, A.; Vogel, V. *Nat. Nanotechnol.* **2008**, *3*, 465–475.
(2) Van den Heuvel, M. G. L.; Dekker, C. *Science* **2007**, *317*, 333–336.
(3) Ebbens, S. J.; Howse, J. R. *Soft Matter* **2010**, *6*, 726–738.
(4) Dreyfus, R.; Baudry, J.; Roper, M. L.; Fermigier, M.; Stone, H. A.; Bibette, J. *Nature* **2005**, *437*, 862–865.
(5) Ghosh, A.; Fischer, P. *Nano Lett.* **2009**, *9*, 2243–2245.
(6) Calvo-Marzal, P.; Sattayasamitsathit, S.; Balasubramanian, S.; Windmiller, J. R.; Dao, C.; Wang, J. *Chem. Commun.* **2010**, *46*, 1623–1624.
(7) Chang, S. T.; Paunov, V. N.; Petsev, D. N.; Velev, O. D. *Nat. Mater.* **2007**, *3*, 235–240.
(8) Ibele, M.; Mallouk, T. E.; Sen, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 3308–3312.
(9) Wang, Y.; Hernandez, R. M.; Bartlett, D. J.; Bingham, J. M.; Kline, T. R.; Sen, A.; Mallouk, T. E. *Langmuir* **2006**, *22*, 10451–10456.
(10) Ismagilov, R. F.; Schwartz, A.; Bowden, N.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 652–654.
(11) Wang, J.; Manesh, K. M. *Small* **2010**, *6*, 338–345.
(12) Zacharia, N. S.; Sadeq, Z. S.; Ozin, G. A. *Chem. Commun.* **2009**, 5856–5858.
(13) Solovev, A. A.; Mei, Y.; Ureña, E. B.; Huang, G.; Schmidt, O. G. *Small* **2009**, *5*, 1688–1692.
(14) Howse, J. R.; Jones, R. A. L.; Ryan, A. J.; Gough, T.; Vafabakhsh, R.; Golestanian, R. *Phys. Rev. Lett.* **2007**, *99*, 048102.
(15) Gibbs, J. G.; Zhao, Y. P. *Appl. Phys. Lett.* **2009**, *94*, 163104.
(16) Pantarotto, D.; Browne, W. R.; Feringa, B. L. *Chem. Commun.* **2008**, 1533–1535.
(17) Mano, N.; Heller, A. *J. Am. Chem. Soc.* **2005**, *127*, 11574–11575.
(18) Stock, C.; Heureux, N.; Browne, W. R.; Feringa, B. L. *Chem.—Eur. J.* **2008**, *14*, 3146–3153.
(19) Fleischmann, M.; Ghoroghchian, J.; Rolison, D.; Pons, S. *J. Phys. Chem.* **1986**, *90*, 6392–6400.
(20) Warakulwit, C.; Nguyen, T.; Majimel, J.; Delville, M.-H.; Lapeyre, V.; Garrigue, P.; Ravaine, V.; Limtrakul, J.; Kuhn, A. *Nano Lett.* **2008**, *8*, 500–504.
(21) Loget, G.; Larcade, G.; Lapeyre, V.; Garrigue, P.; Warakulwit, C.; Limtrakul, J.; Delville, M.-H.; Ravaine, V.; Kuhn, A. *Electrochim. Acta* **2010**, *55*, 8116–8120.
(22) Mavré, F.; Chow, K.-F.; Sheridan, E.; Chang, B.-Y.; Crooks, J. A.; Crooks, R. M. *Anal. Chem.* **2009**, *81*, 6218–6225.
(23) Ordeig, O.; Godino, N.; Del Campo, J.; Muñoz, F. X.; Nikolajeff, F.; Nyholm, L. *Anal. Chem.* **2008**, *80*, 3622–3632.
(24) Ulrich, C.; Andersson, O.; Nyholm, L.; Björefors, F. *Anal. Chem.* **2009**, *81*, 453–459.
(25) Sridevi, R.; Curtis, S. *Langmuir* **2010**, *26*, 4602–4606.
(26) Bradley, J.-C.; Crawford, J.; Ernazarova, K.; McGee, M.; Stephens, S. G. *Adv. Mater.* **1997**, *9*, 1168–1171.
(27) Bouchet, A.; Descamps, E.; Mailley, P.; Livache, T.; Chatelain, F.; Haguet, V. *Small* **2009**, *5*, 2297–2303.
(28) Bradley, J.-C.; Babu, S.; Carroll, B.; Mittal, A. *J. Electroanal. Chem.* **2002**, *522*, 75–85.
(29) Argoul, F.; Kuhn, A. *J. Electroanal. Chem.* **1993**, *359*, 81–96.

JA107644X