Comment on "A Linear Actuation of Polymeric Nanofibrous Bundle for Artificial Muscles"

Sir: Gu et al.[1] have fabricated an electrochemical actuator based on a polymeric nanofibrous bundle for use as artificial muscle. It is well known that the actuation of intrinsically conducting polymers is due to the movement of ions and solvent in and out of the polymer during oxidation and reduction processes.[2] Thus, as a part of electrochemical studies, the cyclic voltammetric behavior has been interpreted by the classic Randles−Sevcik equation. However, the system under consideration does not fulfill the basic assumptions made in the derivation of the Randles−Sevcik equation.[3−5]

The system under consideration is too complicated, from the electrochemical point of view. Different mechanisms have been proposed to explain the pseudo-capacitive behavior of conducting polymers;[6] however, there is no well-defined (commonly accepted) mechanism, because various processes are involved. Similar to other supercapacitors, both the faradaic and nonfaradaic capacitances are responsible for an electrochemical capacitive behavior. Although the role of nonfaradaic capacitance is usually ignored in comparison with capacitance formed by a redox process; the nonfaradaic capacitance is still noticeable,[7] particularly for nanostructured materials with large surface areas. On the other hand, the electrochemical behavior of a conducting polymer is not limited to interfacial processes, and the counterions also diffuse inside the electroactive films.

In general, several processes are responsible for the current recorded in a voltammogram. Thus, this peak current is different from the peak current of a simple redox process addressed in the Randles−Sevcik equation.

It is evident that two different processes are involved in the system under consideration: (i) diffusion within the electrolyte solution toward the electrode surface and (ii) solid-state diffusion inside the electroactive film. Therefore, it is not easy to attribute the diffusion coefficient in the Randles−Sevcik equation to one of these diffusion processes, because both of them dominantly exist in the system under consideration.

As a result, an unrealistic value has been calculated in ref 1 for the diffusion coefficient, i.e., 2.3×10^{-4} cm^2/s. The diffusion coefficient for an electroactive species diffusing in electrolyte solution is of the order of 10^{-6} cm^2/s, and the diffusion coefficient for a solid-state diffusion is normally $< 10^{-8}$ cm^2/s.

To use the Randles−Sevcik equation, compliance with the following conditions is mandatory, because the equation has been originally derived by making these assumptions:

(1) Diffusion is one-dimensional from bulk solution toward the electrode surface.

(2) Diffusion coefficient is constant, because the medium in which diffusion occurs is a uniform supporting electrolyte (inside the Nernst diffusion layer).

(3) Only one simple redox process is involved, because the Nernst equation should be solved for that redox system to derive the Randles−Sevcik equation.

(4) The current is merely attributed to a faradaic process. For analytical purposes, it is even necessary to consider the background current.

Obviously, the system under consideration does not fulfill any of these vital conditions, and, consequently, the Randles−Sevcik equation cannot be applied to interpret the voltammetric behavior of this system.

Another problematic issue is related to the analysis of cyclic voltammetric data. The Randles−Sevcik equation is valid for reversible electrochemical systems displaying characteristic sharp peaks with a peak-to-peak separation close to the theoretical value of 59 mV. However, the system under consideration hardly shows a distinguishable peak. Nicholson and Shain[5] have discussed, both theoretically and experimentally, that, if there is even a slight deviation from the theoretical peak-to-peak separation (for ideally reversible systems), the Randles−Sevcik equation should be modified. It is well-known that the diffusion coefficient is potential-dependent;[8] moreover, the Randles−Sevcik equation considers the diffusion coefficient at the peak potential (which is normally close to the equilibrium potential, at which the Nernst equation is valid), not across a wide potential window. In addition, the specific current recorded at a scan rate of 5 mV/s (as illustrated in Figure 3a in the original paper[1]) is not in consistent with the values reported in Figure S2 in that paper's supplemental data.

As the authors quoted,[1] "the high porosity observed in the hybrid nanofibrous bundle allowed the efficient diffusion of ions and the high surface area provided by the individual nanofibers in the bundles along with the growth of nanostructured polyaniline wires grown on the surface of the highly aligned bundles were

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responsible for the higher electrochemical actuation". Thus, it is of particular importance to estimate a realistic value for the diffusion coefficient, because readers (researchers) can compare the performance of this electrochemical actuator with those of available ones.

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