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Microcontainers with Electrochemically Reversible Permeability

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Elaboration of effective solutions for generation and consumption of electric energy is one of the major challenges for sustainable world development.[1] This also concerns the development of new materials for electrochemical systems with unusual properties and improved output characteristics. Highly sophisticated nanostructured alloys, mesoporous metals, carbon nanotubes, and metal clusters were recently investigated as perspective components of electrochemical systems.[2]

Among other techniques, a facile and cheap approach to the fabrication of nanoengineered electrodes is the layer-by-layer (LbL) technique. Here, a substrate is exposed to solutions of charged species (e.g., polyelectrolytes) enabling the deposition of a film of exceptional homogeneity and high conductivity with thickness and composition controlled on nanoscale level.[3] LbL-designed electrodes were tested in electrochromic applications, catalysis, electroluminescent devices, electrochemically stimulated gene transfer systems, membranes, and fuel cells.[4] If the LbL assembly procedure is performed on the surface of microparticles, polyelectrolyte capsules of defined size and shape can be obtaibed.[5] Polyelectrolyte capsules possess tunable functionality and, especially, the possibility to encapsulate materials and to control mass transport through the shell by ionic strength, pH, temperature, or post chemical reaction.[6]

A number of conductive polymers (e.g., polypyrrole, polyaniline) were developed as prospective electrode materials.[7] Their good conductivity, chemical stability, and mechanical properties allow one to employ conductive polymers as host matrixes for polyelectrolyte capsules developed of composite material, which can combine electric conductivity of the polymer with controlled permeability of polyelectrolyte shell.

The present study demonstrates a novel application of polyelectrolyte microcapsules as microcontainers with electrochemically reversible flux of redox active materials into and out of the capsule volume. Incorporation of the capsules inside the conducting polymer (polypyrrole, PPy) film results in a new composite electrode combining electrocatalytic and conducting properties of the PPy with the storage and release properties of the capsules. This electrode, if loaded with electrochemical fuels, can possess electrochemically controlled switching between "open/closed" states of the capsule shell and be of practical interest for chemically rechargeable batteries or fuel cells operating on an absolutely new concept.

Polyelectrolyte capsules were fabricated by the alternating adsorption of poly(diallyldimethylammonium chloride) (PDADMAC, eight layers) and poly(styrene sulfonate) (PSS, eight layers) onto the surface of 4.5 μm silica particles as previously described.[5] Fluorescein-labeled dextran (FITC-dextran, MW $\approx$ 50000) and poly(hexyl viologen) (PHV, for preparation protocol, see ref 3) were loaded inside PDADMAC/PSS capsules by the thermal encapsulation method:[6b] empty capsules were mixed with polymers (2 mg/mL) in 0.01 M KCl for 1 h, incubated at 55 °C for 20 min, and then washed (see Figure S1). The elevated temperature results in capsule shrinkage up to 2.2 μm and shell densification, which prevents spontaneous release of entrapped dextran or PHV into water or electrolyte solution employed for electrochemical measurements (0.01 M KCl).

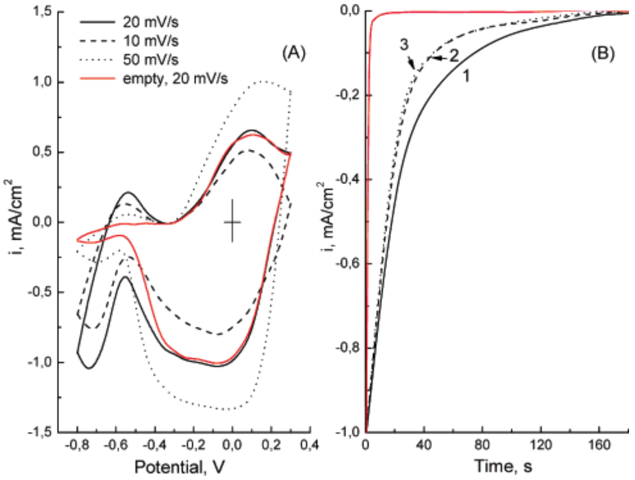

Figure 1. (A) Cyclic voltammograms (cathodic scan direction, initial potential −0.05 V) of polypyrrole electrode impregnated by microcapsules either empty (red) or loaded with PHV (black) at different scan rates. (B) Reductive current vs time dependencies after a potential switch from −0.3 to −0.9 V for a PHV-PPy/microcontainer electrode (black) at subsequent release-reloading cycles: (1) initial PHV-loaded microcapsules; (2) microcapsules electrochemically refilled after discharging of (1); (3) microcapsules refilled after discharging of (2). Red − empty PPy/microcontainer electrode. Reference was SCE.

Films of capsule-containing polypyrrole were produced by oxidation of pyrrole on ITO electrode (from $\sim 10^9$/mL suspension of loaded capsules in 0.05 M pyrrole + 0.01 M KCl at pH = 3) under a potential control at +0.70 V vs saturated calomel electrode (SCE). The film thickness estimated from the charge passing during the electropolymerization was 3.2 μm.[7c]

The mechanism of the capture of the capsules inside the PPy matrix is predominantly adsorption followed by the occlusion by the growing PPy film.[8] Capsules are randomly distributed inside polypyrrole (see Figure S2) and have a packing density of about 5.1×10^6 capsules per cm^2. No detachment of the capsules was observed during washing or electrochemical potential cycling.

Cyclic voltammetry was employed to investigate the electrochemically stimulated release of PHV from the capsule interior. The redox response of the composite electrode (Figure 1A) is the combination of that observed previously for polypyrrole films in aqueous solutions[7] and flat LbL films containing PHV.[4a] Redox peaks in the range of −0.3 to +0.4 V correspond to the processes inherent to the polypyrrole matrix.[7] By decreasing the electrode potential, a sharp redox wave appears at −0.6 V for PHV-loaded capsules, which is perfectly matched to the first reduction/oxidation process of PHV.[4a] This electrochemical signal can indicate the potential-induced opening of the capsule shell accompanied by the release of the PHV. The dependence of the peak heights on the scan rate confirms slow PHV diffusion through the microcontainer

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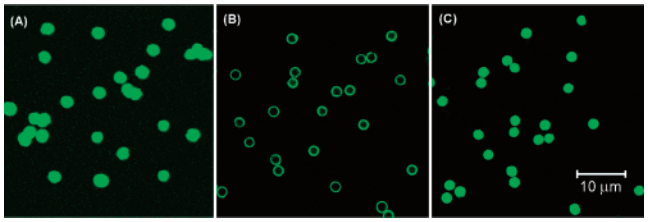

Figure 2. Fluorescent confocal images of polypyrrole electrode film impregnated by microcapsules (A) loaded with FITC-labeled dextran, (B) microcapsules dislodged at −0.9 V, and (C) microcapsules refilled in dextran solution at +0.2 V. The electrode was washed several times by distilled water to eliminate the fluorescent signal from FITC-dextran adsorbed on PPy surface during release/reloading cycles.

shell. This suggests that the polyelectrolyte shell is not completely in "open" state and only a limited number of defects, which could be contact places between polypyrrole matrix and occluded capsule, are formed. Moreover, the quantity of these defects depends on the potential scan rate. Increasing the scan rate to 50 mV/s results in the pronounced decrease of peak heights (Figure 1A) caused by a decreased diffusion of PHV through the shell. Hence, one can conclude that the electrochemically induced opening of the polyelectrolyte capsule is a slow process with the time scale controlled by the potential value and the scan rate.

Chronoamperometry analysis was performed to investigate the response time and electrochemically stimulated reloading of the PPy/microcontainer system. The release and reduction of PHV from the initial PHV-loaded PPy/microcontainer electrode and an electrode after one and two reloading cycles (the disposed electrode was immersed in 2 mg/mL PHV +0.01 M KCl at +0.2 V for 20 min and then fully washed) are compared in Figure 1B. The highest current density was observed for the initial PHV-loaded PPy/microcontainer electrode. Reloading of the abandoned capsules with a new PHV portion is accompanied by a 25% decrease of the charge for the first reloading cycle, whereas no changes were observed for the following four reloading cycles. That can be explained by the irreversible shell distortion and opening for a part of the capsules in PPy matrix at −0.9 V potential. This "broken" part does not participate in the further release/reloading cycles. The maximal number of release/reloading cycles without loosing electrode functionality was 14.

The release/reloading cycles of the PPy/microcontainer system were visualized by fluorescence confocal microscopy employing FITC-labeled dextran as a probe. As shown in Figure 2, the initial dextran-loaded PPy/microcontainer electrode demonstrates high uptake yield in solution without applied potential bias. Changing an electrode potential to −0.9 V for 5 min results in the disappearance of the fluorescent signal from the capsule interior (Figure 2B), which confirms the release of the encapsulated material as shown previously for PHV. The fluorescence was only observed from the capsule shell where dextran is adsorbed within the polyelectrolyte multilayers and cannot be released into the polypyrrole matrix as compared to freely floating dextran entrapped in the capsule interior.[6]

Hollow polyelectrolyte capsules can be reloaded with new portions of FITC-dextran from a 2 mg/mL solution at positive potential bias. Tweny minutes of incubation at +0.2 V were sufficient to reload PDADMAC/PSS capsules inside a PPy/microcontainer electrode (Figure 2C). The incubation time or release time can be reduced by increasing the potential bias (for example, 12 min is the minimal time for capsule reloading at +0.45 V). However, larger potential step leads to the destruction of the capsule shell, and its inability for electrochemically induced reversible permeability changes, which is in a good agreement with the results of chronoamperometry measurements for encapsulated PHV.

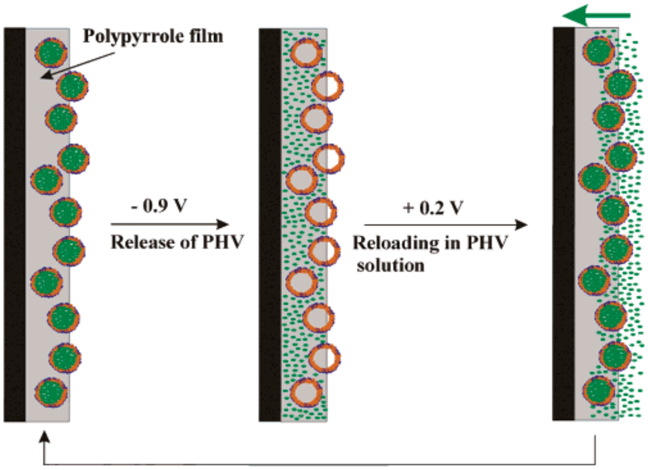

Figure 3. Schematic representation of the functioning of the resulting polypyrrole/microcontainer electrochemical system.

In conclusion, we demonstrated for the first time a new concept of an electrode system able to self-regulate the quantity of the materials (fuels) involved in the electrochemical process. A general function scheme of the composite PPy/microcontainer system is illustrated in Figure 3. Changing the electrochemical potential of the polypyrrole allows the control of the efficiency of redox process. The dislodged PPy/microcontainer system can be reversibly reloaded by the same or different redox active material, which can be employed in a new generation of chemically rechargeable accumulators. A special explanation for the potential-dependent loading and unloading may be related to the fact that the capsules experience a potential gradient and PPy conformational changes within which the polyions of the capsule shell can be moved. In the future, the demonstrated approach will be utilized for the development of fuel cells providing a discrete, controlled supply of electrochemical fuels dispersed at the nanolevel.

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Supporting Information Available: Description of the encapsulation method and microscopy images of a polypyrrole/microcontainer electrode. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Marechal, F.; Jochem, E. *Resour. Conserv. Recycl.* **2005**, *44*, 245−262.
(2) (a) McKenzie, K. J.; Marken, F.; Oyama, M.; Gardner, C. E.; Macpherson J. V. *Electroanal.* **2004**, *16*, 89−96. (b) Frey, T.; Friedrich, K.; Garche, J. *J. Electrochem. Soc.* **2005**, *152*, A545−A551.
(3) (a) Ferreira, M.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7107−7114. (b) Laurent, D.; Schlenoff, J. B. *Langmuir* **1997**, *13*, 1552−1557.
(4) (a) DeLongchamp, D. M.; Kastantin, M.; Hammond, P. T. *Chem. Mater.* **2003**, *15*, 1575−1586. (b) Kurth, D. G.; Lopez, J. P.; Dong W. F. *Chem. Commun.* **2005**, 2119−2121. (c) Yan, X. D.; Ji, H. F.; Lvov Y. *Chem. Phys. Lett.* **2004**, *396*, 34−37. (d) Olek, M.; Ostrander, J.; Kotov, N.; Giersig, M. *Nanoletters* **2004**, *4*, 1889−1895.
(5) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S.; Möhwald, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2202−2205.
(6) (a) Shchukin, D. G.; Sukhorukov, G. B. *Adv. Mater.* **2004**, *16*, 671−682. (b) Köhler, K.; Shchukin, D. G.; Sukhorukov, G. B.; Möhwald, H. *J. Phys. Chem. B* **2005**, *109*, 18250−18259.
(7) (a) Chiang, C. K.; Park, Y. W.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098−1101. (b) Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139−182. (c) Grzeszczuk, M.; Zabinska, G. *J. Electroanal. Chem.* **1997**, *427*, 169−177.
(8) Zhou, M.; Rajeshwar, K. *J. Electroanal. Chem.* **1997**, *421*, 111−120.

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