CROATICA CHEMICA ACTA CCACAA **71** (4) 1127–1137 (1998)

ISSN-0011-1643
CCA-2553

Original Scientific Paper

Preparation and Utilization of Self-assembled Ultrathin Films Composed of Polyelectrolytes, Nanoparticles and Nanoplatelets

Janos H. Fendler

Center for Advanced Materials Processing, Clarkson University,
P. O. Box 5814, Potsdam, New York 13699–5814, USA

Received May 2, 1998; accepted July 7, 1998

The layer-by-layer self-assembly of polyelectrolytes, colloidal nanoparticles and nanoplatelets provides a convenient route to the construction of ultrathin films with many potential applications. The utility of this approach is illustrated by describing the construction of a high energy density rechargeable lithium-ion battery.

THE IMPORTANCE OF SIZE QUANTIZATION OF PARTICLES AND PLATELETS

Colloid chemists have traditionally dealt with dispersed particles, usually in the micrometer to submicrometer range. More recently their attention has focused upon nanometer regime. The construction of nanostructured materials by »wet« colloid chemical methods has been inspired by mother nature's organizational ability.[1] Nanostructured materials are synthesized in nature by a process known as biomineralization (the *in vivo* formation of inorganic crystals and/or amorphous particles in biological systems).[2–4] Biomineralization is believed to be mediated by proteins acting as templates at membrane interfaces.

Nanosized or nanostructured materials have dimensions, as their name implies, in the 1–100 nanometer range. Nanosized materials are described

---

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

in terms of size quantization. Size quantization occurs at dimensions comparable to the length of the de Broglie electron, the wavelength of phonons, and the mean free path of excitons.[5–7] Electron-hole confinement in nanosized, spherical semiconductor particles results in three-dimensional size quantization, *i.e.*, in the formation of »quantum dots«, »quantum crystallites«, or »zero-dimensional excitons«. Two-dimensional confinement of the charge carriers results in »quantum well wires«, »quantum wires«, or »one-dimensional excitons« (*i.e.*, the exciton is provided with only one-dimensional mobility). Finally, in one-dimensional size quantization, the exciton is permitted to move in two-dimensions (»two-dimensional excitons«) with the resultant formation of »quantum wells«. Band-gap engineering by size and dimension quantization is important since it leads to mechanical, chemical, electrical, optical, magnetic, electro-optical, and magneto-optical properties which are substantially different from those observed for the bulk material.[5–7] For example, quantum dots can be tuned by changing their diameters to absorb and emit light at any desired wavelength. This property makes it feasible to construct a finely tunable and efficient semiconductor laser.[8] Semiconductor quantum dots can, in principle, be designed to capture a single electron at a time.[9,10] Exploitation of this concept will open the door for the manufacturing of ultrahigh density integrated circuits and information storage devices which are based on the presence or absence of individual electrons.

Clay minerals and graphite are naturally occurring platelets. Smectic clays, such as Na^+-montmorillonite, have been exfoliated into (10 ± 2) Å thick layered silicates, often referred to as clay organocomplexes, by ion exchange reaction with cationic surfactants.[11,12] The high lateral bond strength and aspect ratios have rendered clay organocomplexes to be eminently suitable materials for nanoconstruction. Indeed, the nanocomposites prepared by mixing polymers and clay organocomplexes had superior mechanical properties.[13]

SELF-ASSEMBLY OF POLYELECTROLYTES, NANOPARTICLES AND NANOPLATELETS

Exploitation of the beneficial properties of nanoparticles and nanoplatelets for device construction requires that they be organized into high density, two dimensional, arrays and/or three dimensional networks in which suitable electrical contact can be made and in which the current, voltage and/or light intensity can be measured. Only ordered arrays of homogeneous nanoparticles are expected to have a resonance interaction and long range periodicity of their spacial arrangements and hence only they are expected to have the efficient nonlinear response which is required in many electrical and electro-optical applications.

The term »self-assembly« implies the spontaneous adsorption of molecules or of nanoparticles, in a monoparticularly thick layer, onto a substrate. Self-assembled multilayer films are formed by the absorption of subsequent monolayers of molecules or nanoparticles. The evolution of self-assembled layers of molecularly nanostructured materials can be traced, at least conceptually, from simple surfactant monolayers and multilayers, through their more complex particulate analogues to the self-assembly of simple molecules and larger particulates.

The layer-by-layer self-assembly of polyelectrolyte – nanoparticles (or nanoplatelets) onto substrates is deceptively simple. A well cleaned substrate is primed by adsorbing a layer of surfactant or polyelectrolyte onto its surface. The primed substrate is then immersed into a dilute aqueous solution of a cationic polyelectrolyte, for a time optimized for adsorption of a monolayer, rinsed and dried. The next step is the immersion of the polyelectrolyte monolayer covered substrate into a dilute dispersion of negatively charged nanoparticles (or nanoplatelets), also for a time optimized for adsorption of a monoparticulate layer, rinsing and drying. These operations complete the self-assembly of a polyelectrolyte monolayer – monoparticulate layer of nanoparticle (or nanoplatelet) sandwich onto the primed substrate. Subsequent sandwich units are deposited analogously (Figure 1).

Absorption and emission spectrophotometry, surface plasmon spectroscopy, X-ray diffractometry, scanning force microscopy and transmission electron microscopy have been used for monitoring the self-assembly and characterizing the structures of self-assembled films.[11]

Self-assembly of nanoparticles to the oppositely charged substrate surface is governed by a delicate balance of the adsorption and desorption equilibria. The efficient adsorption of one (and only one) monoparticulate layer of nanoparticles onto the oppositely charged substrate surface is the objective of the immersion step. Preventing the desorption of the nanoparticles during the rinsing process is of equal importance. The optimization of the self- assembly in terms of maximizing the adsorption of nanoparticles from their dispersions and minimizing their desorption on rinsing requires the judicious selection of stabilizer(s) and the careful control of the kinetics of the process. The self-assembly of CdS and PbS nanoparticles was found to be most efficient, for example, if the semiconductor particles were coated by a 1 : 3 mixture of thiolactic acid and ethyl mercaptane.[11] It has to be admitted that this composition of the capping agent was arrived at by many trial and error experiments.

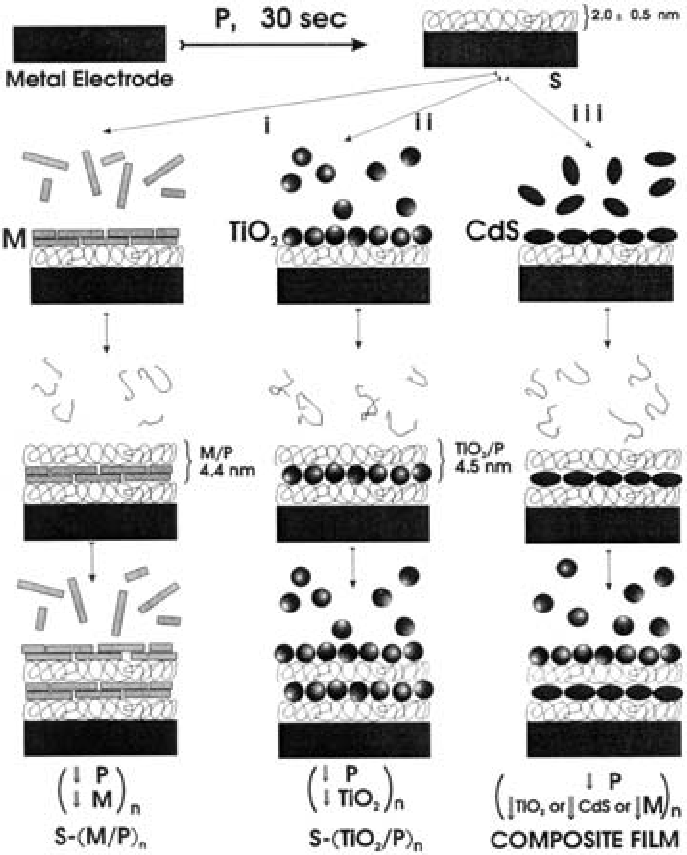

Figure 1. Spontaneous self-assembly of composite nanostructured films. A well cleaned substrate is primed by adsorbing a layer of cationic polyelectrolyte onto its surface. The primed substrate is then immersed into a dilute dispersion of surfactant-coated, negatively charged semiconductor nanoparticles (or clay platelets or graphite oxide) for a time optimized for adsorption of a monoparticulate layer, rinsed and dried to form an organic-inorganic sandwich unit. Subsequent sandwich units are deposited analogously.

UTILIZATION OF SELF-ASSEMBLED FILMS

The relative ease of preparation and the high degree of versatility render self-assembled ultrathin films amenable to a large variety of diverse applications. Self-assembled films can function as membranes (barriers), with controllable levels of permeability, for gases, liquids, covalent molecules, ions and, indeed, for electrons (tunneling barriers). These properties have been exploited for the construction of insulators, passivators, sensors and modified electrodes. Self-assembled nanostructured films are eminently suitable for the construction of devices based on molecular recognition. Molecules or supramolecular assemblies (nanoparticles) within a self-assembled layer can be aligned spontaneously, or by changing the temperature, pressure and pH, or, alternatively and additionally, by the application of an electric or magnetic field. These characteristics permit the formation of superlattices with desired symmetry (or dissymmetry) and, hence the fabrication of a host of photonic, electronic, magnetic and non-linear optical devices. The layer-by-layer self-assembly of insulators (appropriate hydrocarbon surfactants, for example), conductors (metallic nanoparticles, graphite, conducting polymers, for example), magnetic, ferroelectric and semiconductors nanoparticulate films, in any desired order, allows the construction of molecularly (or supramolecularly) resolved heterostructures. These, in turn, afford the optimization of charge separation and carrier transport to the level necessary for the band-gap engineering of quantum devices. Control of the sizes and interparticle distances of the monodispersed nanoparticles within the self-assembled film can be exploited for such optical applications as the construction of Bragg diffraction devices for Raman spectrometers and for enhancing the Raman intensity by surface plasmon interactions.[14] Other applications are likely to be developed.

Recent exploitation in our laboratories of self-assembled films is illustrated by the construction of a high energy density rechargeable lithium-ion battery. The operation of lithium-ion batteries is deceptively simple.[15,16] Charging is accomplished by the insertion of lithium-ions and electrons into an intercalation compound which serves as the positive electrode. When the battery is discharged lithium-ions are de-intercalated and electrons are released through the external circuit as energy. The circuit is completed by a negative electrode (lithium metal, for example) and the current is conducted by lithium ions, aided by an inert supporting electrolyte ($LiAsF_6$, for example), in an anhydrous organic solvents (methyl formate + ethylene carbonate, for example). The electrochemical potential difference between the two electrodes determines the storable voltage for a given lithium-ion battery and the storage capacity is governed by the number of lithium-ions that can be reversibly intercalated into a given electrode volume. The high densities and storage capacities required for such consumer electronic products as camcorders, cameras and computers are responsible for the ever increasing demand for more efficient lithium-ion batteries.[17–19] Using high-capacity carbonaceous materials and graphite as intercalation electrodes and assuming that one lithium-ion is inserted per six carbon atoms (*i.e.*, Li_1C_6) it should be possible to produce a battery with a specific capacity of 372 mAh g^{-1}, which corresponds to energies between 100 – 150 Wh kg^{-1} and energy densities between 250–400 Wh l^{-1}, Ref 19. To further increase the energies and energy densities of lithium-ion batteries it is necessary to decrease the size of graphite to the nanometer size regime (*i.e.,* to form graphenes) and thereby to generate additional sites for lithium-ion intercalation. Surprisingly, no synthetic strategies have been developed for the formation of active graphite nanoplatelets with controllable reactivity for use as intercalation electrodes in lithium-ion batteries.

We launched an entirely new approach for the construction of a high capacity intercalating cathode by self-assembling[20–25] nanometer thick polyelectrolytes and graphite oxide/graphite nanoplatelets. In this approach, charging and discharging have been determined in a three-electrode electrochemical cell (Figure 2).[26] The working electrode has been fabricated by self-assembling poly(diallyldimethyl-ammonium) chloride, PDDA, GO nanoplatelets, and poly(ethylene oxide), PEO, onto transparent indium tin oxide, ITO. Lithium wires have served as the anode and the counter electrode. The cell has contained $LiASF_6$ as a supporting electrolyte and methyl formate and ethylene carbonate as solvent. Positively charged PDDA has been chosen as the »building-polymer« since it is known to interact strongly with negatively charged GO nanoplatelets by electrostatic forces and thus it fa-

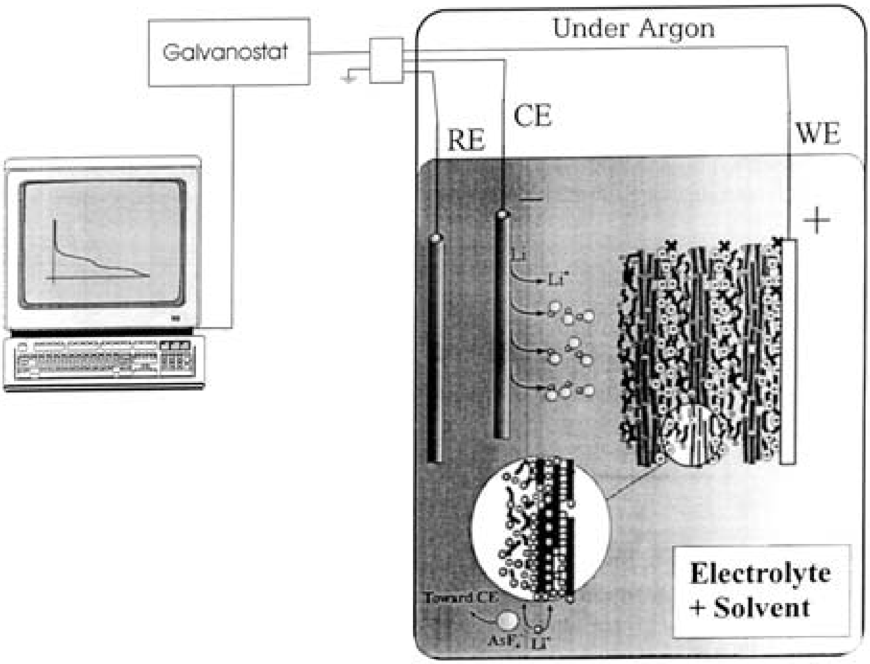

Figure 2. Revised electrochemical cell.

cilitates the quantitative self-assembly of these nanolayers onto a conductive substrate.[12] PEO, an ion-conducting polymer, have synergized the »building«function of the polyelectrolyte by allowing further layer-by-layer growth of the films.[26]

Ultrathin films of S-$(PDDA/GO)_{10}$ (Film **I)** S-PDDA$(GO/PEO)_{10}$, (Film **II**), S-$(PDDA/GO/PEO)_{10}$ (Film **III**), S-$(PDDA/PEO)_{10}$ (Film **IV**), and S--$(PDDA/MO/PEO)_{10}$ (Film **V**)[27] were self-assembled and characterized by absorption spectra, cyclic voltammetry, voltage *vs.* capacity plots (charging and discharging), XRD and AFM. The regular growth of the films was established by the observed linear plots of the absorbances at 230 nm against the number of sandwich units self-assembled. Modification of the topologies and thicknesses of the GO layers were assessed by AFM (Figure 3). Average thicknesses of 80 ± 12 Å for Film **I** and 70 ± 12 Å for Film **III** were determined for the GO layer on top of the polyelectrolytes, with a significant coverage. However, an average thickness of only 20 ± 7 Å and a lower coverage were observed for GO layered onto PEO (Film **II**).

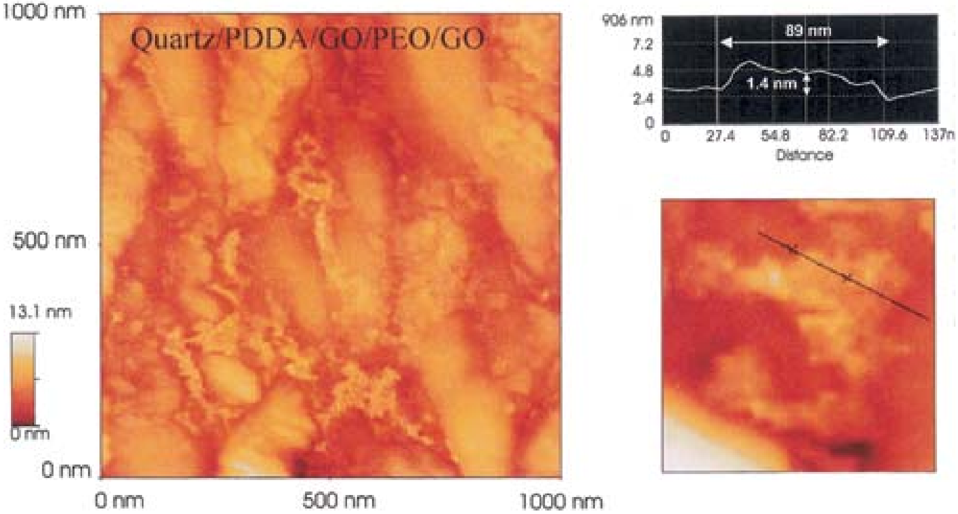

Figure 3. AFM image of a GO layer standing on the top of a polyoxyethylene layer in the system S-$(PDDA/GO/PEO)_n$, also shown, a close view of a GO nanoplatelet of about 14 A thick.

Charging and discharging were determined by standard voltage *vs.* capacity measurements (Figure 4) in an electrochemical cell (Figure 2). In all

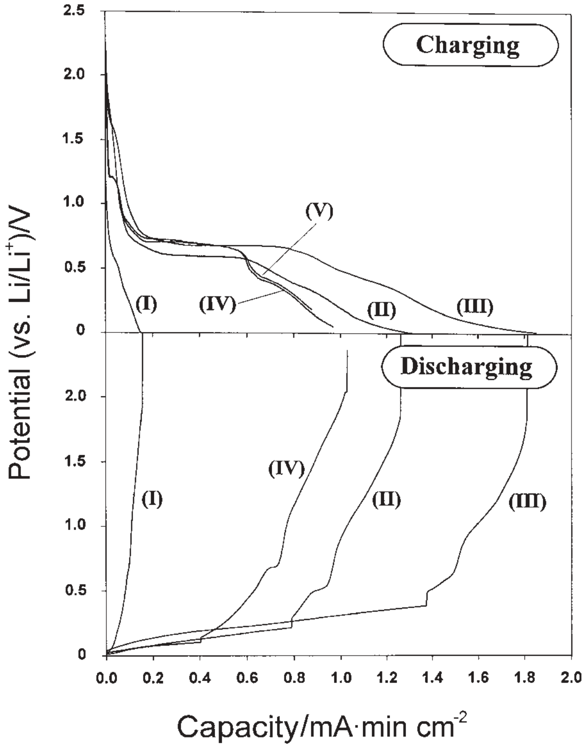

Figure 4. Current charge and discharge curves obtained for the five self-assembled systems, relatively to a lithium reference electrode.

cases, a full reversibility of the charging processes was observed, but interestingly, the main plateaus appeared at lower potentials during the current discharge (*ca.* + 0.3 V *vs.* Li/Li$^+$) than during the current charge (*ca.* + 0.7 V *vs.* Li/Li$^+$) indicating that these two processes may be governed by different mechanisms. In spite of the fact that Film **I** contained the largest amount of GO, the charging was the smallest, indicating that using a positively charged electrolyte (PDDA) hindered the insertion of Li$^+$ ions. In order to improve the penetration of Li$^+$ ions into the multilayers, each GO layer was sandwiched between a layer of PDDA and a layer of PEO (Film **III**) or, alternatively, GO was sandwiched between PEO only and self-assembled onto a PDDA coated substrate (Film **II**). The very high specific capacities of Films **II** and Films **III** (1232 and 1134 mAh g^{-1}) are likely to originate in the facilitated transport of Li$^+$ to the vicinity of the GO nanoplatelets by PEO. The activity of these GO layers was also demonstrated by determining the charging capacity of a film in which GO was replaced by montmorillonite

(MO) platelets (Film **V**). Charging of Film **V,** relative to Film **IV**, was found to be negligible, demonstrating the crucial importance of GO in the intercalation of lithium-ions.

Concomitant with lithium-ion insertion GO was found to reduce to graphite, G. Conversion of GO to G occurred at a potential of +2.6 V *vs.* Li/Li$^+$, as determined by cyclic voltammetry. It should be noticed that charging started at a less positive potential (+2.2 V, Figure 4). Contribution of PEO was evaluated to be 0.105 mA min/cm^2 by comparing the charging (or discharging) of Film **IV** and Film **V**. Subtracting this contribution from the charging determined for Film **II** and Film **III** resulted in a linear relationship between charging and the amount of GO incorporated into the films (the ratios of [Q/C cm^{-2} – 0.105] : [total thickness of the GO layers] for Film **II** and Film **III** were almost identical: 8.5×10^{-5} and 8.7×10^{-5}, respectively).

Insertion of lithium-ions during the charging caused a dramatic change in the absorption spectra of the films, they became progressively blacker paralleling the GO to G conversion. Importantly, more than 92% of the charging and 73% of the discharging occurred at a potential below 0.65 V for Film **II** and Film **III**, making them particularly attractive as candidates for low voltage rechargeable batteries. Most remarkably, values of the reversible specific capacity of the graphite layers in these films (1174 mAh g^{-1} and 1232 mAh g^{-1}) were much higher than the highest specific capacities (500–770 mAh g^{-1})[28] reported for carbonaceous materials or that for polyacenic semiconductor (PAS) materials (1100 mAh g^{-1}).[29] The batteries prepared here (based on Film **II** and Film **III**) exhibited a significant hysteresis with respect to potential but had fully reversible capacity even on the first charging. We attribute this high performance capacity to the presence of stacked graphite nanoplatelets (with high surface areas) which are in contact with PEO (Figure 1). A lithium to carbon ratio of compound LiC_2 is only achievable with small diameter graphene sheets,[30,31] suggesting that the oxidative treatment leading to GO generated important edge modifications and disruptions of the conjugation length, leading to smaller graphitic domains. Using the self-assembled submicron thick S-(PDDA/GO/PEO)$_{10}$ electrode (Film **III**), prepared in this work, we have discovered a new route to the nanofabrication of fully reversible Li-ion batteries. Furthermore, our electrochemical cell can be readily scaled up to an economically viable »solid state« high capacity rechargeable lithium ion battery.

CONCLUSION

The outlook for colloid chemistry is bright. We have learned how to prepare monodispersed nanoparticles and nanoplatelets. The challenge is now to treat them as if they were simple molecules, derivatize them and construct two-dimensional arrays and three-dimensional networks which will function as novel sensors and devices.

Acknowledgment. – Support of this work by the New York State Science and Technology Foundation and Clarkson University's Center for Advanced Materials Processing (CAMP) is gratefully acknowledged.

REFERENCES

1. S. Mann, *Biomimetic Materials Chemistry,* VCH, New York, 1996.
2. S. Mann, *Nature* **365** (1993) 499–505.
3. L. Addadi and S. Weiner, *Angew. Chem., Int. Ed. Engl.* **31** (1992) 153–169.
4. B. R. Heywood and S. Mann, *Advan. Mater.* **6** (1994) 9–20.
5. V. L. Colvin, A. N. Goldstein, and A. P. Alivisatos, *J. Am. Chem. Soc.* **114** (1992) 5221–5230.
6. A. Henglein, *Ber. Bunsenges. Phys. Chem.* **99** (1995) 903–913.
7. G. Hodes, *Solar Energy Materials and Solar Cells – A Review,* **34** (1994) 323.
8. V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, *Nature* **370** (1994) 354–357.
9. M. H. Devoret, D. Esteve, and C. Urbina, *Nature* **360** (1992) 547–552.
10. K. Nakazato and H. Ahmed, *Advan. Mater.* **5** (1993) 668–671.
11. N. A. Kotov, I. Dékány, and J. H. Fendler, *J. Phys. Chem.* **99** (1995) 13065–13069.
12. N. A. Kotov, I. Dékány, and J. H. Fendler, *Advan. Mater.* **8** (1996) 637–641.
13. T. Lan and T. J. Pinnavaia, *Chem. Mater.* **6** (1994) 2216–2219.
14. S. A. Asher, J. Holtz, L. Liu, and Z. Wu, *J. Am. Chem. Soc.* **116** (1994) 4997–4998.
15. J. R. Owen, *Chem. Soc. Rev.* **26** (1997) 259–267.
16. G. Pistoia, (Ed.), *Lithium Batteries – New Materials, Developments and Perspectives*, Elsevier, Amsterdam, 1995.
17. J. M. Tarascon and D. Guyomard, *Electrochim. Acta* **38** (1993) 1221–1231.
18. P. G. Bruce, *Philos. Trans. R. Soc. London, A* **354** (1996) 1577–1593.
19. K. M. Abraham, *Electrochim. Acta* **38** (1993) 1233–1248.
20. S. W. Keller, H. N. Kim, and T. E. Mallouk, *J. Am. Chem. Soc.* **116** (1994) 8817–8818.
21. S. W. Keller, S. A. Johnson, E. S. Brigham, E. H. Yonemoto, and T. E. Mallouk, *J. Am. Chem. Soc.* **117** (1995) 12879–12880.
22. Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *J. Am. Chem. Soc.* **117** (1995) 6117–6123.
23. G. Decher, *Comprehensive Supramolecular Chemistry,* in: J.-P. Sauvage (Ed.), *Layered Nanoarchitectures* via *Directed Assembly and Anionic and Cationic Molecules,* Vol. 9, Pergamon Press, Oxford, 1996, pp. 507–528.
24. J. H. Fendler, *Chem. Mat. 8* (1996) 1616–1624.
25. G. Decher, *Science* **277** (1997) 1232–1237.
26. T. Cassagneau and J. H. Fendler, *Advan. Mater.* **10** (1998) 877–882.

27. S. Sato, M. Noguchi, A. Demachi, N. Oki, and M. Endo, *Science* **264** (1994) 556–559.
28. J. S. Sue, K. Myrthe, and J. R. Dahn, *J. Electrochem. Soc*. **142** (1995) 2927–2929.
29. a) S. Yata, H. Kimoshita, M. Komoi, N. Ando, T. Kashiwamura, T. Harada, K. Tanaka, and T. Yamabe, *Synth. Met*. **62** (1994) 153–156;
    b) S. Yata, Y. Hato, H. Kinoshita, N. Ando, A. Anekawa, T. Hashimoto, M. Yamaguchi, K. Tanaka, and T. Yamabe, *Synth. Met*. **73** (1995) 273–279 ;
    c) H. Ago, K. Tanaka, T. Yamabe, K. Takegoshi, T. Terao, S. Yata, Y. Hato, and N. Ando, *Synth. Met*. **89** (1997) 141–147.
30. T. Zheng, Y. H. Liu, E. W. Fuller, S. Tseng, U. Vonsacken, and J. R. Dahn, *J. Electrochem. Soc.* **142** (1995) 2581–2590.
31. A. Gerouki, M. A. Goldner, R. B. Goldner, T. E. Haas, T. Y. Liu, and S. Slaven, *J. Electrochem. Soc.* **143** (1996) L262–L263.

SAŽETAK

Priprava i primjena ultratankih filmova sastavljenih od polielektrolita, nano-čestica i nano-pločica

Janos H. Fendler

Postupno i slojevito nanošenje polielektrolita, koloidnih nanometarskih čestica i pločica pogodan je način priprave ultratankih filmova. Ti filmovi imaju brojne primjene. Prednost ovog načina priređivanja filmova prikazana je na primjeru litijeva članka visoke gustoće energije koji se po pražnjenju može ponovno puniti elektrikom.