Available online at www.sciencedirect.com
ScienceDirect
Electrochimica Acta 51 (2006) 6038–6044
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Study on charge transfer reactions at multilayers of polyoxometalates clusters and poly(allylamine hydrochloride) (Grotthuss-018)

N. Gu [a,1], D. Wei [a,c], L. Niu [a,b], A. Ivaska [a,*,2]

[a] *Laboratory of Analytical Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo-Turku, Finland*
[b] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*
[c] *Graduate School of Materials Research, Åbo Akademi University, FIN-20500 Åbo-Turku, Finland*

Received 18 July 2005; received in revised form 10 January 2006; accepted 16 January 2006
Available online 5 May 2006

Abstract

Multilayers of anionic phosphotungstic acid (PTA) clusters and positively charged protonated poly(allylamine hydrochloride) (PAH) were assembled by layer-by-layer self-assembled method on Au electrode modified by 3-mercaptopropionic acid (3-MPA). The effect of the charge of the surface of the multilayer assembly on the kinetics of the charge transfer reaction was studied by using the redox probes $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$. The cyclic voltammetry experiments showed that the peak currents and peak-to-peak potential differences changed after assembling different layers on the electrode surface indicating that the charge of the surface has a significant effect on the kinetics of the studied charge transfer reactions. These reactions were studied in more detail by electrochemical impedance spectroscopy. When $[Fe(CN)_6]^{3-/4-}$ was used as the redox label, multilayers that terminated with negatively charged PTA showed a high charge transfer resistance but multilayers that terminated with positively charged PAH showed lower charge transfer resistance. With $[Ru(NH_3)_6]^{2+/3+}$ as the redox label, the charge transfer resistance at multilayers that terminated with positively charged PAH was much higher than at the multilayer terminated by the negatively charged PTA. The charge transfer resistances also increased with the addition of number of layers indicating that the entire thickness of the multilayer assembly has also an effect on the kinetics of the studied charge transfer reactions and not only the electrostatic attraction or repulsion between the surface and the redox probes. The ohmic resistance of the multilayer assembly increased non-linearly with the number of layers. Assembling a layer of PAH increased the resistance more than assembling a layer of PTA.

Keywords: Nanostructures; Polyoxometalates; Multilayer; Layer-by-layer method; Electrochemical impedance spectroscopy

1. Introduction

In recent years, multilayers have extensively been studied since they can be used to design and build different types of molecular architectures and study physical phenomena on a molecular level [1–3]. Preparation techniques of multilayer films via stepwise adsorption from solution have been developed rapidly in the last decade [4–6]. The developed methods give different possibilities to assemble various multilayer films containing polymers, nanoparticles, two-dimensional inorganic sheets and molecular aggregates [7–9]. The structure and thickness of such films can be controlled by molecular precision.

Advanced material based on inorganic nanoparticles is currently one of the key research fields of today's materials science. They represent significant fundamental and commercial interests with a wide range of applications including optics, electronic and sensors [10–12]. Layer-by-layer (LBL) method based on electrostatic interaction between oppositely charged materials is an effective way to assemble nanocomposite layers [13–18]. The diversity in materials has led to their extensive applications in molecular architectures with novel functionalities. Furthermore, by properly chosen charged compounds, a variety of multilayer films with interesting functional properties become easily accessible. LBL method can be considered as a convenient, simple and quite universal method to process nanoparticles and related

* Corresponding author. Tel.: +358 2 2154420; fax: +358 2 2154479.
E-mail address: ari.ivaska@abo.fi (A. Ivaska).
[1] Present address: Department of Chemistry, Nanchang University, Nanchang 330047, PR China.
[2] ISE member.

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.01.065

materials into a variety of thin-film devices, which opens broad perspectives both in research and in practical applications.

Polyoxometalates (POMs) represent a well-defined class of inorganic compounds with potential applications in fundamental and applied science. Recently, POMs have attracted much attention to fabricate functional composite materials due to their particular interesting nano-sized structures and other applications in heterogeneous catalysis, fuel cell technology, photochromic and electrochromic devices [19,20]. Using LBL techniques, it is feasible to deposit POMs in multilayers and thus to get highly ordered POM arrays even in macroscopic scale.

Multilayers based on POMs, polyelectrolytes and conducting polymers have widely been studied, and many works have been reported [21–26], but only little attention has been focused on characterization of the structure and charge transfer processes in multilayer assemblies. In this paper, we study fabrication of nanocomposite multilayers based on phosphotungstic acid hydrate and poly(allylamine hydrochloride) by the LBL method. The film growth will be studied by cyclic voltammetry and electrochemical impedance spectroscopy with oppositely charged redox probes: $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$. The effect of attraction or repulsion between the redox probes and the multilayer surface on the cyclic voltammograms, film resistances and charge transfer resistances obtained from equivalent circuit, and charge transfer processes at the surface of the assembly will be discussed.

2. Experimental

2.1. Chemicals

Sodium sulfate, potassium hexacyanoferrate(III), potassium hexacyanoferrate(II), hexaammineruthenium(III) chloride, 3-mercaptopropionic acid (3-MPA) and poly(allylamine hydrochloride) (PAH) average molecular weight 15,000 and phosphotungstic acid hydrate (PTA, reagent grade) were purchased from Sigma–Aldrich, and used without further purification. Sodium acetate (regent grade, from Baker Inc.) and acetic acid (≥99.99%, from Aldrich) were used to prepare the buffer solution with pH 5.6. Solutions were prepared from water that had been purified through a Maxima ultrapure water system (ELGA, 18.2 MΩ cm). All solutions were purged with nitrogen prior to use.

2.2. Preparation of the gold electrode

Prior to sputtering the metal films, the microscope glass slides were cleaned with piranha solution (96% H_2SO_4/30% H_2O_2, 7:3), rinsed copiously with water, and dried completely. Then, the Au overlayer (ca. 3000 Å) was coated on glass plates (15 mm × 26 mm) that had pre-covered with a Cr underlayer (ca. 100 Å) by vacuum sputtering deposition (Balzers SCD 50, Germany) at 2×10^{-2} mbar. An underlayer of chromium was used to improve the mechanical stability of the Au film.

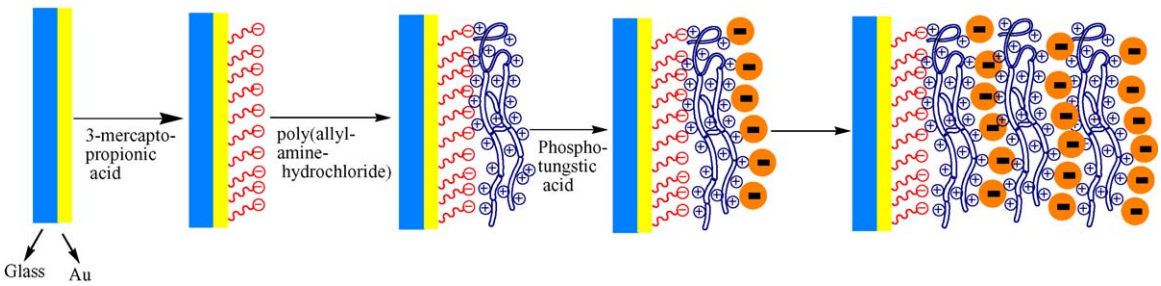
2.3. Preparation of the multilayer

At first, a Au/3-MPA self-assembled monolayer was formed onto a freshly sputtered gold electrode by immersing the electrode in 5 mM 3-MPA solution in 0.1 mol/L acetate buffer of pH 5.6 for 3 h. The electrode was then immersed in 10 mg/mL PAH solutions for 30 min, followed by rinsing with deionized water and dried with nitrogen after the immersion. Then this modified electrode was alternately dipped in the 5 mM PTA and 10 mg/mL PAH solutions for 30 min, rinsed with deionized water and dried in a nitrogen stream after each dipping. Repetition of the adsorption steps leads to the desired number of PAH/PTA bilayers. The surface charge of the multilayer assembly was negative or positive depending on the terminal layer. Formation of multilayers by layer-by-layer deposition of poly(allylamine hydrochloride) and phosphotungstic acid hydrate on 3-mercaptopropionic acid modified gold electrode is described in Scheme 1.

2.4. The electrochemical cell and the measurements

Electrochemical measurements were performed in a three-electrode cell. A platinum wire was used as the counter electrode, and an Ag|AgCl (sat. KCl) electrode as the reference electrode, against which all potentials are reported. The working electrode (sputtered Au film) was placed at a bottom hole of an electrochemical cell with an O-ring (0.8 cm i.d., 0.5 cm^2, perfluoroelastomer, Kalrez, USA).

In the electrochemical impedance spectroscopy (EIS) and cyclic voltammetry measurements, Autolab PGSTAT 20 FRA 2 electrochemical analyzer was used. The EIS measurements were performed within the frequency range of 0.1 Hz–100 kHz. The amplitude of the applied sine wave potential in each measurement was 10 mV. Total 5 mM concentration of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (molar ratio 1:1) and 5 mM $[Ru(NH_3)_6]Cl_3$ in



Scheme 1. Preparation of multilayers based on polyoxometalate clusters and poly(allylamine hydrochloride) onto a 3-MPA modified Au electrode.

0.1 mol/L sodium sulfate solution were used as the redox probes, The dc potential was 220 mV in the case of $[Fe(CN)_6]^{3-/4-}$ and −200 mV in the case of $[Ru(NH_3)_6]^{2+/3+}$.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry was used to study the electrical properties of the multilayer assemblies. Redox reactions of the negatively charged probe $[Fe(CN)_6]^{3-/4-}$ and the positively charged probe $[Ru(NH_3)_6]^{2+/3+}$ were studied at the multilayer surface after adsorption of layers of PAH and PTA. Earlier studies in similar systems have indicated that the electrostatic attraction or repulsion between charged surface and charged redox probes play a significant role during the redox process at a electrode surface [27,28]. Electrostatic attraction between the oppositely charged multilayer surface and the redox probe should enhance the interfacial electron transfer process. On the other hand, however, repulsion between identical charged multilayer surface and the redox probe would make the electron transfer reaction more difficult.

Fig. 1 shows the cyclic voltammograms obtained with different multilayer assemblies when the negatively charged probe $[Fe(CN)_6]^{3-/4-}$ and the positively charged probe $[Ru(NH_3)_6]^{2+/3+}$ were used as the redox species. It can be seen that the cyclic voltammogram (1a) of $[Ru(NH_3)_6]^{2+/3+}$ on 3-MPA modified gold electrode exhibits quasi-reversible redox properties indicating a small charge transfer resistance of the redox process. However, after addition of the positively charged PAH layer the redox peak current of $[Ru(NH_3)_6]^{2+/3+}$ decreases and the cyclic voltammogram (1b) is slightly distorted, which is due to the repulsion between $[Ru(NH_3)_6]^{2+/3+}$ and the positively charged surface of the modified electrode causing slow kinetics of the redox reaction. On the other hand, the peak current of the redox process of $[Fe(CN)_6]^{3-/4-}$ increases when the PAH layer is added (2a and 2b), which is due to attraction between $[Fe(CN)_6]^{3-/4-}$ and the positively charged surface of the modified electrode. It indicates that the kinetics of the charge transfer reaction becomes more facile at the positively charged PAH surface.

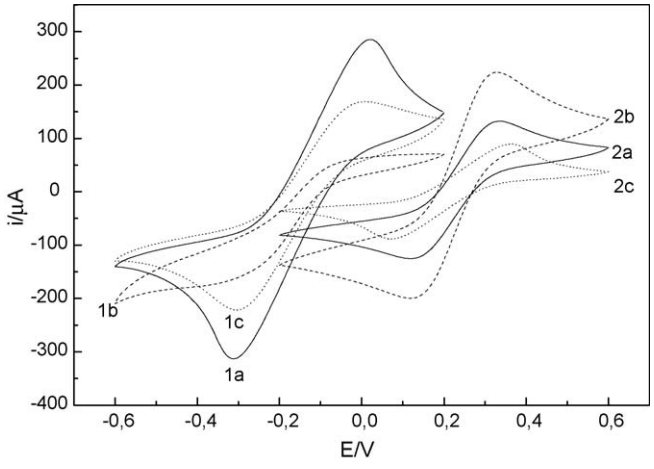


Fig. 1. Cyclic voltammograms in presences of 5 mM $[Ru(NH_3)_6]^{2+/3+}$ at an Au electrode with (1a) monolayer of 3-MPA, (1b) first (outermost) layer of PAH and (1c) first (outermost) layer of PTA; and 5 mM $[Fe(CN)_6]^{4-/3-}$ at an Au electrode with (2a) monolayer of 3-MPA, (2b) first (outermost) layer of PAH and (2c) first (outermost) layer of PTA.

After addition of the negatively charged PTA layer, the redox peak current of $[Ru(NH_3)_6]^{2+/3+}$ increases and cyclic voltammogram shows again quasi-reversible redox behavior (1c), while the redox peak current of $[Fe(CN)_6]^{3-/4-}$ decreases and peak-to-peak separation increases (2c). Similar changes in the voltammograms can be found in building up subsequent multilayers. The changes in peak current and peak-to-peak separation indicate that the electrostatic attractions or repulsions have significant effects on kinetics of the redox reactions either accelerating or decelerating the processes. It was also found that with increasing number of PAH/PTA bilayers the peak current of both redox probes decreased gradually, and the peak-to-peak separation increased, indicating that, in general, kinetics of the redox reactions become more slow.

The assembled multilayers are not perfect in the layer-by-layer sense because the polymer chains are soft and winding and therefore the polymer-polyoxometalate multilayes are not well defined. In the electrochemical point of view the multilayer assemblies, however, were found rather stable because the cyclic voltammetric response did not change even when the electrodes were potential cycled up to 10 cycles. This was found with all the different multilayer assemblies.

3.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a powerful technique to investigate the interfacial properties of modified electrodes. During the step-by-step deposition of charged PAH and PTA layers, the electrical properties of the multilayer assembly is changed. The capacitance, the film resistance, the charge transfer resistance at the interface and the surface charge will be changed during the build-up of the multilayer assembly. In order to study the effect of the structure of the multilayer on the over-all electrochemical properties of the assemblies, electrochemical impedance spectroscopic experiments were conducted after adsorption of each layer of PAH or PTA.

Fig. 2 shows the results of electrochemical impedance spectroscopy studies on multilayer electrodes with different numbers of PAH/PTA layers when $[Fe(CN)_6]^{3-/4-}$ is used as the redox probe. The impedance spectra when $[Ru(NH_3)_6]^{2+/3+}$ is used as the redox probe are shown in Fig. 3. Obvious changes in the impedance spectra can be seen in both figures during the stepwise formation of the multilayer assemblies. A semicircle is observed in the high frequency range in all impedance spectra indicating a process limited by electron transfer. The diameter of the semicircle increases gradually with the increasing number of PAH/PTA bilayers, which should be attributed to the increase in film resistance and variation of charge transfer resistance. As mentioned above, the electrostatic attraction and repulsion between the redox probe and the surface of the multilayer assemblies play a significant role in the charge transfer process.

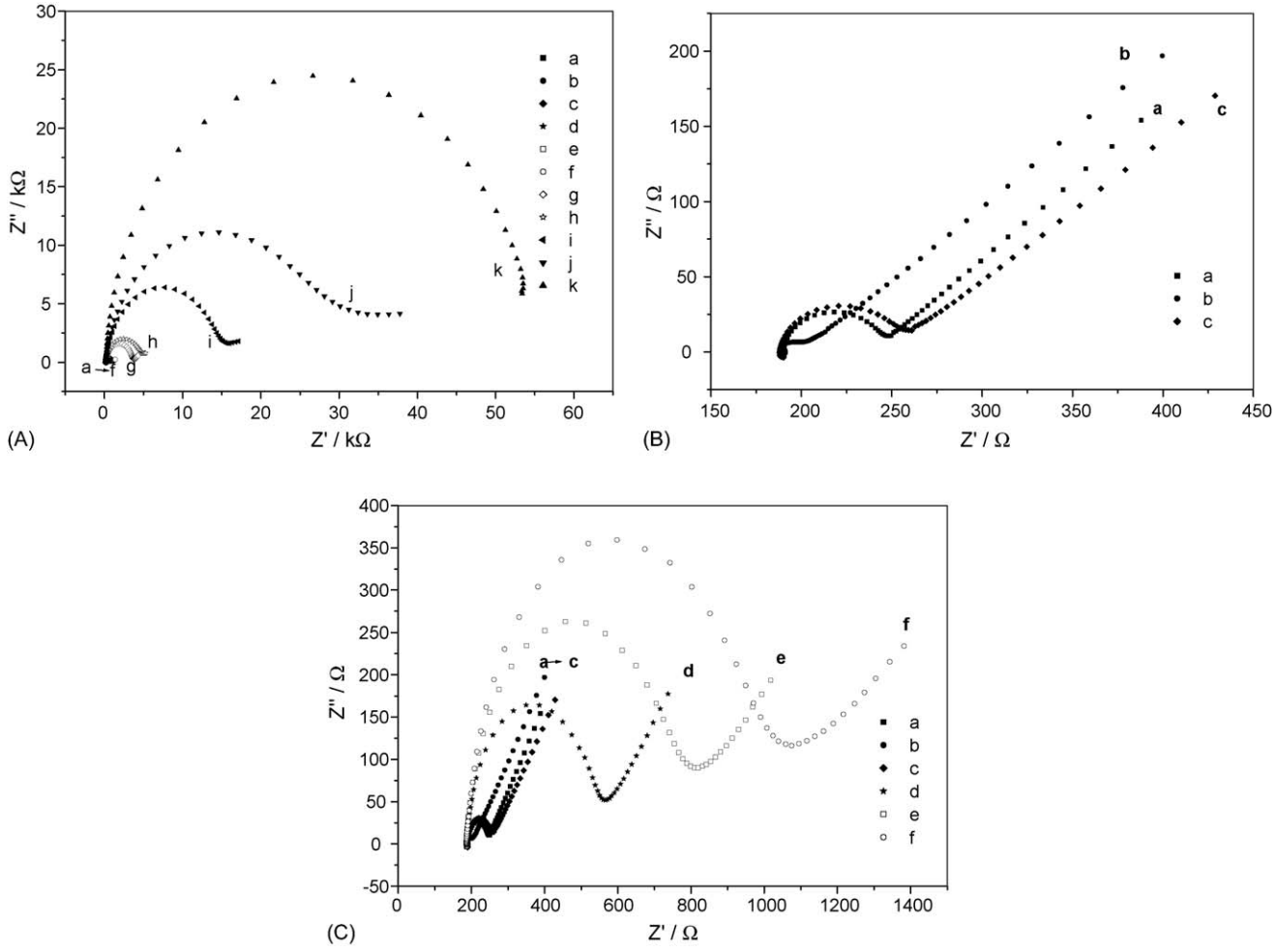


Fig. 2. (A) Nyquist plot for the electrochemical impedance measurements in the presence of 5 mM $[Fe(CN)_6]^{4-/3-}$ redox probe at sputtered Au electrodes terminated with (a) the 3-MPA monolayer, (b) first layer of PAH, (c) first layer of PTA, (d) second layer of PAH, (e) second layer of PTA, (f) third layer of PAH, (g) third layer of PTA, (h) fourth layer of PAH, (i) fourth layer of PTA, (j) fifth layer of PAH and (k) fifth layer of PTA. (B) The enlarged spectra of (a–c). (C) The enlarged spectra of (a–f). The measurements were done at 220 mV and with the amplitude 10 mV in the frequency range from 0.1 Hz to 10 kHz.

In order to obtain quantitative information of the electrochemical parameters involved in formation of the multilayer assembly an electrical equivalent circuit was used. The data of each experimental impedances spectrum were fitted in the circuit shown in Scheme 2. It consists of the ohmic resistance of the solution R_s, the capacitance C_f and the resistance R_f of the multilayer assembly. These parameters depend on the thickness of the film, content and mobility of ions in the film. The double layer capacitance C_{dl} is associated with the surface of the multilayer assembly and R_{ct} is the charge transfer resistance of the redox process that take place at the interface between the solution and the multilayer assembly. Fitting of the data to the equivalent circuit is conducted by Zview software of Scribner Associates, Inc. The values of R_{ct} and R_f found by fitting are shown in Table 1. All five parameters in Scheme 2 are used simultaneously in the fitting procedure.

It can be found in Table 1 that the film resistances of the multilayer assemblies, R_f, are almost the same when both $[Fe(CN)_6]^{3-/4-}$ or $[Ru(NH_3)_6]^{2+/3+}$ are used as the redox probe. This observation shows that the film resistance of the multilayer assemblies mainly depends on the physical structure of the multilayer. The film resistance was neglectable only when the monolayer of 3-MPA was used to modify the Au electrode, and increased only slightly after addition of the first PAH and PTA layers. The structure of the multilayer assembly made by the LBL self-assembled method is affected by many factors including also the number of layers. When only few layers are assembled on the electrode substrate, the surface is not entirely covered by adsorbed materials but consists rather of isolated islands of adsorbed molecules on the substrate. These structures can be described as thin and porous films with low film resistance and not as a compact multilayer assembly entirely covering the electrode surface.

When the number of layers increases the film resistance will be more pronounced and it increases non-linearly with the film thickness indicating formation of a more compact multilayer assembly on the electrode substrate. It can also be found in Table 1 that the increase in the film resistance mainly occurred after assembly of each PAH layer. Adsorption of the PTA layer seems to have only little influence on the film resistance, which is obviously due to the better electric conductivity of the PTA layer. As can be seen in Table 1 the film resistance values obtained with

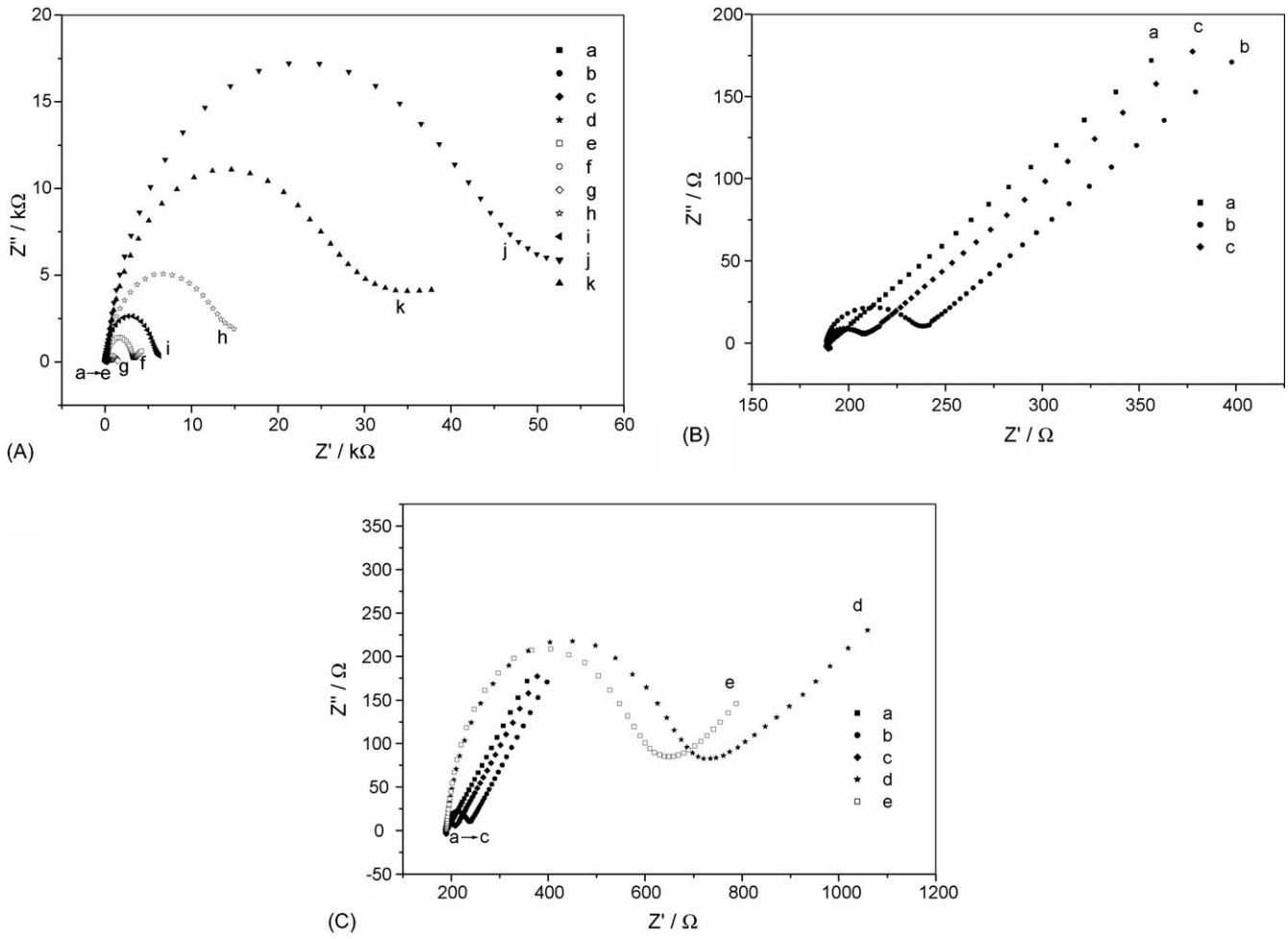


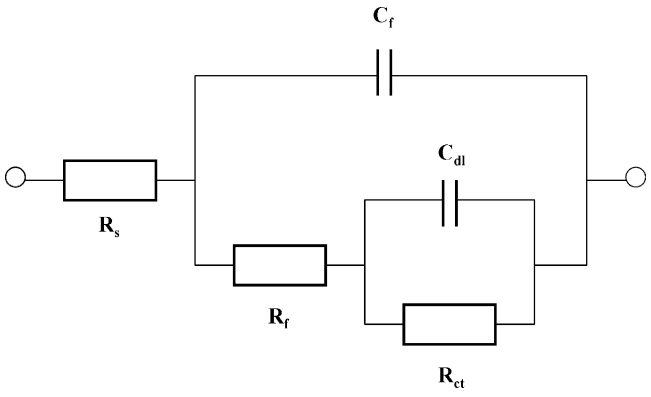
Fig. 3. (A) Nyquist plots for the electrochemical impedance measurements in presence of 5 mM $[Ru(NH_3)_6]^{2+/3+}$ redox probe at sputtered Au electrodes terminated with (a) the 3-MPA monolayer, (b) first layer of PAH, (c) first layer of PTA, (d) second layer of PAH, (e) second layer of PTA, (f) third layer of PAH, (g) third layer of PTA, (h) fourth layer of PAH, (i) fourth layer of PTA, (j) fifth layer of PAH and (k) fifth layer of PTA. (B) The enlarged spectra of (a–c). (C) The enlarged spectra of (a–e). The measurements were done at −200 mV with the amplitude of 10 mV in the frequency range from 0.1 Hz to 10 kHz.

both redox probes for the same multilayer assemblies are the same within the experimental errors verifying the proper fitting procedure.

It can be seen in Figs. 2 and 3 and Table 1 that after modification of the Au substrate by the 3-MPA monolayer the charge transfer resistance with $[Fe(CN)_6]^{3-/4-}$ as the redox probe is higher than that with $[Ru(NH_3)_6]^{2+/3+}$. The observed difference in the charge transfer resistances is due to the electrostatic attraction and repulsion of the redox probes with the negatively charged substrate. After addition of the first PAH layer the surface charge is reversed, which causes changes in the interaction between the charged redox probes and the surface

Table 1
Charge transfer resistances R_{ct} and film resistances R_f, obtained from the impedance spectra of the multilayer assemblies in the presence of 5 mM $[Fe(CN)_6]^{4-/3-}$ and 5 mM $[Ru(NH_3)_6]^{2+/3+}$ redox probes upon fitting the experiment data with the equivalent circuit shown in Scheme 2

Assembly terminated with	R_{ct} (kΩ) ($[Fe(CN)_6]^{4-/3-}$)	R_f (kΩ) ($[Fe(CN)_6]^{4-/3-}$)	R_{ct} (kΩ) ($[Ru(NH_3)_6]^{2+/3+}$)	R_f (kΩ) ($[Ru(NH_3)_6]^{2+/3+}$)
Monolayer of 3-MPA	0.058	∼0	∼0	∼0
First layer of PAH	0.003	0.009	0.032	0.008
First layer of PTA	0.066	0.012	0.012	0.014
Second layer of PAH	0.021	0.365	0.14	0.351
Second layer of PTA	0.27	0.380	0.038	0.362
Third layer of PAH	0.084	0.86	2.15	0.84
Third layer of PTA	2.74	0.94	0.12	0.88
Fourth layer of PAH	0.41	4.53	8.46	4.32
Fourth layer of PTA	9.28	5.03	0.54	4.69
Fifth layer of PAH	0.62	28.4	20.6	27.7
Fifth layer of PTA	23.6	29.2	1.21	28.3



Scheme 2. The equivalent circuit for the PAH/PTA multilayers. R_s is the ohmic resistance of the solution, C_f the film capacitance, R_f the film resistance, R_{ct} the charge transfer resistance and C_{dl} is the double layer capacitance.

of the electrode. The charge transfer resistance decreases with $[Fe(CN)_6]^{3-/4-}$ and increases with $[Ru(NH_3)_6]^{2+/3+}$. Adsorption of the next layer, negatively charged PTA, reverses the surface charge again and the electrostatic interaction creates repulsion of the negatively charged $[Fe(CN)_6]^{3-/4-}$ ions making the charge transfer reaction at the surface more difficult. Attraction between the positively charged $[Ru(NH_3)_6]^{2+/3+}$ and the negatively charged surface makes the charge transfer reaction at the surface more facile. These explanations are supported by the impedance spectra shown in Figs. 2 and 3, and the charge transfer resistance values shown in Table 1. The charge transfer resistance increases from 3 to 66 Ω after adsorption of the first PTA layer when $[Fe(CN)_6]^{3-/4-}$ is used as the redox probe, and decreases from 32 to 12 Ω while $[Ru(NH_3)_6]^{2+/3+}$ is used as the redox probe.

After the second layer of PAH is assembled, the value of the charge transfer resistance decreases and increases when $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$ are used as the redox probes, respectively. This is again due to the different electrostatic interaction between the charged redox probes and the positively charged multilayer assembly surface. Adsorption of the second, negatively charged layer of PTA again increases the charge transfer resistance with $[Fe(CN)_6]^{3-/4-}$ and decreases it with $[Ru(NH_3)_6]^{2+/3+}$. Similar types of changes in the charge transfer resistance are observed with addition of the further layers.

It can also be found in Table 1 that the charge transfer resistance increases with increasing number of PAH/PTA bilayers both with $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$. The increase in charge transfer resistance with both redox probes is not linear and the difference in the charge transfer resistance after addition of new bilayers becomes larger indicating that thicker multilayers make charge transfer reactions also more difficult. As described above, when only few layers are added on the electrode substrate, the assembly can be regarded as a thin and porous structure. It is then possible for the studied redox probes to penetrate the multilayer and to undergo redox reactions directly at the electrode surface and therefore the charge transfer resistances is also low. Along with the growth of multilayers, the thickness of the layer assembly increases and the ion diffusion process becomes more difficult in the compact multilayers and therefore the redox reactions mainly take place at the interface between the multilayer assembly and the electrolyte. In these cases, the charge transfer process is affected by the thickness of the multilayer assembly and the charge transfer resistance is increased with the increasing thickness of the film.

4. Conclusions

Electrostatic interactions between the surface of the multilayer assemblies and the redox probes affect the charge transfer reaction at the surface. The results presented in Table 1 show that: (i) during growth of the multilayer assemblies, while multilayer assembly is terminated with negatively charged PTA layer, repulsion between $[Fe(CN)_6]^{3-/4-}$ ions and the multilayer surface causes the high charge transfer resistance. The attraction between $[Ru(NH_3)_6]^{2+/3+}$ ions and the multilayer surface makes the charge transfer reaction easier. While multilayer assembly is terminated with positively charged PAH layer, the charge transfer resistance increases when $[Ru(NH_3)_6]^{2+/3+}$ is used as the redox probe and decreases when $[Fe(CN)_6]^{3-/4-}$ is used. (ii) For a certain multilayer assembly, the charge transfer resistance of oppositely charged redox probe to the charge of the multilayer surface is always lower than that of the same charged redox probe. (iii) When the redox probes have the same charge as the multilayer surface, the charge transfer resistance increases sharply with the increase of the number of multilayers. When the redox probes have the opposite charge than the multilayer, the charge transfer resistance is much lower and increases only slowly with the number of multilayers. (iv) The thickness of the multilayer assembly has also an effect on the charge transfer reaction at the multilayer surface obviously due to the increased ohmic resistance of the entire multilayer assembly. Results in Table 1 show that the film resistance increases non-linearly with the number of multilayers, and the increase in the film resistance mainly occurred after the addition of each PAH layer.

Acknowledgments

This work is a part of the activity of the Åbo Akademi University, Process Chemistry Center, nominated to a National Centre of Excellence (CoE) by the Academy of Finland for (2000–2005). The authors wish to gratefully acknowledge the financial support for the joint project (between LoAC, ÅA, Finland and SKLEAC, CIAC, China) from Academy of Finland and from NSFC, China.

References

[1] G. Decher, J. Schmitt, Prog. Colloid Polym. Sci. 89 (1992) 160.
[2] G.B. Sukhorukov, H. Möhwald, G. Decher, Y.M. Lvov, Thin Solid Film 284/285 (1996) 220.
[3] D.L. Elbert, C.B. Herbert, J.A. Hubbell, Langmuir 15 (1998) 5355.
[4] V. Pardo-Yissar, E. Katz, O. Lioubashevski, I. Willner, Langmuir 17 (2001) 1110.
[5] K. Araki, M.J. Wagner, M.S. Wrighton, Langmuir 12 (1996) 5393.
[6] F. Saremi, G. Lange, B. Tieke, Adv. Mater. 8 (1996) 923.

[7] T. Cassagneau, J.H. Fendler, S.A. Johnson, T.E. Mallouk, Adv. Mater. 12 (2000) 1363.
[8] E.R. Kleinfeld, G.S. Ferguson, Science 265 (1994) 370.
[9] J. Ichinose, K. Fujiyoshi, S. Mizuki, Y. Lvov, T. Kunitake, Chem. Lett. (1996) 257.
[10] A.P. Alivisatos, J. Phys. Chem. 100 (1996) 13226.
[11] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, Science 281 (1998) 2013.
[12] W.C.W. Chan, S. Nie, Science 281 (1998) 2016.
[13] M.A. Correa-Duarte, M. Giersig, N.A. Kotov, L.M. Liz-Marzan, Langmuir 14 (1998) 6430.
[14] J.W. Ostrander, A.A. Mamedov, N.A. Kotov, J. Am. Chem. Soc. 123 (2001) 1101.
[15] G.S. Ferguson, E.R. Kleinfeld, Adv. Mater. 7 (1995) 414.
[16] C.M. Bell, M.F. Arendt, L. Gomez, R.H. Schmehl, T.E. Mallouk, J. Am. Chem. Soc. 116 (1994) 8374.
[17] Y. Liu, Y. Wang, R.O. Claus, Chem. Phys. Lett. 298 (1998) 315.
[18] E. Hao, T. Lian, Langmuir 16 (2000) 7879.
[19] T. Yamase, Chem. Rev. 98 (1998) 359.
[20] Y. Guo, Y. Wang, C. Hu, Y. Wang, E. Wang, Y. Zhou, S. Feng, Chem. Mater. 12 (2000) 3501.
[21] L. Cheng, L. Niu, J. Gong, S. Dong, Chem. Mater. 11 (1999) 1465.
[22] L. Cheng, J. Cox, Electrochem. Commun. 3 (2001) 285.
[23] P.J. Kulesza, M. Chojak, K. Karnicka, K. Miecznikowski, B. Palys, A. Lewera, A. Wieckowski, Chem. Mater. 16 (2004) 4128.
[24] K. Karnicka, M. Chojak, K. Miecznikowski, M. Skunik, B. Baranowska, A. Kolary, A. Piranska, B. Palys, L. Adamczyk, P.J. Kulesza, Bioelectrochemistry 66 (2005) 79.
[25] L. Adamczyk, P.J. Kulesza, K. Miecznikowski, B. Palys, M. Chojak, D. Krawczyk, J. Electrochem. Soc. 152 (2005) E98.
[26] A. Lewera, G. Zukowska, K. Miecznikowski, M. Chojak, W. Wieczorek, P.J. Kulesza, Anal. Chim. Acta 536 (2005) 275.
[27] F. Malem, D. Mandler, Anal. Chem. 65 (1993) 37.
[28] E. Katz, D.D. Schlereth, H.L. Schmidt, J. Electroanal. Chem. 367 (1994) 59.