Fabrication of highly ordered macroporous copper films using template-assisted electrodeposition in an ionic liquid

S. Zein El Abedin a,b,c,⁎, A. Prowald a,b, F. Endres a,b

a Institute of Particle Technology, Arnold-Sommerfeld-Str. 6, Clausthal University of Technology, D-38678 Clausthal-Zellerfeld, Germany
b EFZN (Energieforschungszentrum) Goslar, Am Stollen 19, 38640 Goslar, Germany
c Electrochemistry and Corrosion Laboratory, National Research Centre, Dokki, Cairo, Egypt

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In the present communication we report on the electrochemical synthesis of highly ordered macroporous copper films in the ionic liquid 1-butyl-3-methylimidazolium dicyanamide [BMim]DCA using polystyrene (PS) templates. The polystyrene colloidal spheres are arranged onto gold and indium tin oxide substrates in an ordered hexagonal structure. The interstitial voids of the PS sphere arrays are subsequently filled with copper by electrodeposition. After chemical dissolution of the PS spheres well ordered macroporous copper films were obtained. Depending on the experimental parameters, highly ordered 2- and 3-dimensional macroporous Cu films with interconnected pore structure can be made. The macroporous Cu films showed diffractive colours by varying the angle of the incident light.

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1. Introduction

Macroporous materials have gained extensive attention for their widespread applications [1–4]. The template-assisted electrodeposition technique is the most common approach for synthesis of macroporous materials. As copper is an important catalyst, the synthesis of highly ordered macroporous copper films can lead to improved catalytic performance of Cu catalysts. Templated electrodeposition of macroporous copper films from aqueous electrolytes using gas bubbles as a dynamic template [5] or sea urchin electrodeposition of macroporous lead to improved catalytic performance of Cu catalysts. Templated the synthesis of highly ordered macroporous copper films showed diffractive colours by varying the angle of the incident light.

electrolytes. They showed that ordered macroporous Cu films can only be obtained in aqueous electrolytes after hydrophilic modification of the PS template by sodium dodecyl sulfate prior to electrodeposition [8]. The surface tensions of most ionic liquids with imidazolium cations are between 25 and 49 mN.m−1 [9,10], which are well below that of water (72.8 mN/m [11]), and hence a better infiltration of the interstitial voids of PS spheres by the ionic liquid electrolyte is expected. Chen et al. [12] employed ionic liquid electrolytes for electrodeposition of ordered macroporous silver films using PS templates. They found that ionic liquids exhibit better wetting on the hydrophobic PS templates than aqueous electrolytes. Template-directed electrodeposition of highly ordered macroporous germanium films in the ionic liquid 1-butyl-1-methylpyrrolidinum bis[trifluoromethylsulfonyl] amide was also reported [13].

2. Experimental

The electrodeposition of macroporous copper was studied in the ionic liquid [BMim]DCA with high purity (Io-Li-Tec). The ionic liquid was used as received without further purification or drying. The viscosity, density and surface tension of the employed ionic liquid at 20 °C were reported to be 39.14 mPa.s [14], 1.066 g.cm−3 [14] and 48.6 mN.m−1 [15], respectively. The water content determined by Karl–Fischer titration was found to be 640 ppm. The water content has a direct influence on the physical properties of the employed ionic liquid. For example, the increase in water content in [BMim]DCA leads to a significant decrease in the viscosity and to a minor decrease in the density...
No information is available on the effect of water on the surface tension of [BMIm]DCA. However, it was reported that the water content has a little influence on the surface tension of ionic liquids [16]. Therefore, it can be stated that the presence of some water residual does not significantly influence the wettability of the PS spheres and hence the quality of the deposit would not be affected. Copper (I) chloride (Alfa, 99.999%) was used as a source of copper. Polystyrene (PS) spheres with 600 nm diameter (Duke Scientific) suspended in pure ethanol (10 vol.% PS in ethanol) were used to prepare the templates on gold-sputtered and on indium tin oxide (ITO)-coated glass substrates. The PS templates were prepared by dipping the substrates into the polystyrene suspension for a few seconds at 40 °C. Due to self-assembly, the PS spheres arrange onto the surface of the employed substrates in an ordered hexagonal structure.

All electrochemical measurements were performed in an argon filled glove box using a Potentiostat/Galvanostat 263A (Princeton Applied Research) controlled by PowerCV and PowerStep software. The electrochemical cell was made of polytetrafluoroethylene (Teflon®) and clamped over a Teflon® covered Viton o-ring onto the working electrode, thus yielding a geometric surface area of 0.3 cm². A copper ring (Alfa, 99.99%) and a copper wire (Alfa, 99.99%) were used as counter and reference electrodes, respectively. The surface morphology of the electrodeposited macroporous copper films was investigated using a high resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini).

3. Results and discussion

Monodispersed colloidal polystyrene spheres with sizes of 600 nm are ordered into hexagonal close-packed arrays by self-assembly on the employed substrates. A typical SEM micrograph of an ordered PS spheres array on gold as a template for electrochemical synthesis of macroporous copper films is shown in Fig. 1a. As seen, the PS spheres are well ordered into close-packed domains with a few point and line defects in the sphere arrays. No significant disordered regions were observed all over the surface, the obtained arrays are ordered over centimetre scales. It should be noted that the microstructure of the electrodeposited porous films is strongly dependent on the arrangement of the PS spheres on the substrate. Generally, close-packed PS spheres arrays yield highly ordered macroporous films.

The cyclic voltammetry behaviour of the PS template formed on gold was investigated in the ionic liquid [BMIm]DCA containing 0.2 mol/l CuCl, Fig. 1b. The potential was swept in the negative direction from the open circuit potential (ocp) to −0.4 V (vs. Cu), then scanned back to +0.9 V and finally stopped at the ocp. Two pronounced redox processes were observed. The first redox process
c1/a1 is associated with Cu deposition/stripping, while the second redox couple a2/c2 is ascribed to the oxidation of Cu(I) to Cu(II) at a2 and its subsequent reduction at c2. A small current loop was observed when the scan was reversed indicating a nucleation process.

The electrodeposition of copper from the employed ionic liquid in the voids of the PS spheres was done potentiostatically by applying potentials of $-0.15\, \text{V}$ and of $-0.2\, \text{V}$ for 6 and 10 min, respectively. The applied potentials were chosen to be slightly more negative than the starting deposition potential of Cu in order to control the rate of Cu deposition. A successful fabrication of highly ordered macroporous films is strongly dependent on the applied potential and on the deposition time as high negative applied potential, i.e. high deposition rate, might lead to non-ordered porous film. Also, a prolonged deposition time leads to overgrowing of the deposit on the top of outermost PS layer forming a continuous film. Prior to electrodeposition experiments, the PS-Au template was kept in the employed ionic liquid electrolyte for about 10 min to ensure complete infiltration into the voids of the PS spheres. Once a potential is applied, the deposition of Cu starts directly on the gold surface unoccupied by PS spheres until formation of a first layer. By ongoing time the Cu deposit grows three dimensionally, layer by layer, from the gold surface towards the solution to fill the interstitial voids of the PS templates. After removing the PS template by chemical dissolution in tetrahydrofuran (THF), highly ordered macroporous Cu films were obtained with pores similar in size as PS spheres. The SEM micrographs of Fig. 2 show a 2D-macroporous Cu film obtained at a potential of $-0.15\, \text{V}$ for 6 min. The low magnification SEM micrograph, Fig. 2a, displays a representative topography of the obtained sample showing ordered macroporosity over a large surface area. The higher magnification SEM micrograph of Fig. 2b reveals a perfectly ordered 2D-macroporous Cu film with uniform interconnected pores and a long-term periodicity. The obtained 2D-macroporous Cu sample shows diffractive colours when illuminated with white light. By varying the angle of the incident light the sample displays different colours, Fig. 2c. The colour of the films changes due to the diffraction of light by the periodic macroporous structure. In periodic structures the light diffracts when the periodicity approaches the wavelengths of visible light producing different colours [17].
By applying a potential of −0.2 V for 10 min an ordered 3D-macroporous Cu film was made. Fig. 3 manifests two SEM micrographs with different magnifications for the 3D-film. As shown in the SEM micrograph of Fig. 3a, an ordered 3D-macroporous structure with apparent triangular top surface was obtained. The high magnification SEM micrograph of Fig. 3b demonstrates a well ordered macroporous film over a large area. The top layer contains spherical pores with diameters comparable to those of PS spheres. Within these pores three smaller holes are clearly seen from the layer underneath indicating a 3D close-packed macroporous structure.

The electrodeposition of Cu on PS/ITO templates was also investigated. Fig. 4a displays two successive cyclic voltammograms recorded on a PS/ITO electrode in the employed electrolyte. As seen, the electrodeposition of Cu starts at a high negative potential of about −0.65 V, and in the backward scan the cathodic current continues to flow crossing the forward scan at a potential of about −0.1 V forming a pronounced current loop. This indicates that a nucleation process is involved in the electrodeposition of Cu on PS/ITO and a high overpotential is necessary to initiate nucleation and growth. The ratio of the anodic to cathodic charges determined from the integrated peak areas in the cyclic voltammogram is obviously lower than one indicating incomplete stripping of the deposited copper. Therefore, the bulk deposition of Cu in the second scan starts at significantly low negative potential due to the presence of Cu on the electrode surface. In order to obtain a 3D-macroporous Cu film on PS/ITO a constant potential of −0.6 V was applied for 20 min. Fig. 4b depicts a SEM micrograph of the obtained deposit which indicates the formation of an ordered 3D-macroporous Cu film over a large area. The SEM micrograph of Fig. 4c exhibits a highly ordered, multilayered macroporous structure. The top layer comprises hemispherical pores with perfect interconnections and high periodicity. In the light of the above results it can be stated that highly ordered 2D- and 3D-macroporous Cu films can be made in the ionic liquid [BMIm]DCA due to its high wettability and penetrability through the voids of the PS templates. Catalytic applications would benefit from the high surface area and porous structure of macroporous Cu films. The photonic characteristics of such films suggest their potential in optical applications. Furthermore, application of 3D-macroporous Cu films as a current collector in Li ion batteries to host the anode material may offer a possible solution to the bad cyclability resulting from the large volume expansion during lithiation.

4. Conclusions

We have shown that highly ordered macroporous Cu films can be made in the ionic liquid [BMIm]DCA using polystyrene templates. The employed ionic liquid showed complete infiltration into the voids of the PS template. Depending on the experimental parameters, 2- and 3-dimensional macroporous Cu films with interconnected pores and a long range periodicity were obtained. The films showed a colour change when illuminated with white light resulting from the diffraction of light by the well ordered macroporous structure. The attractive surface and optical characteristics make such films potential candidates for diverse applications.

References
