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Electrochemical Method for Direct Deposition of Nanometric Bismuth and Its Electrochemical Properties vs Li

Alexandre Finke,^a Philippe Poizot,^{a,z} Claude Guéry,^a Loïc Dupont,^{a,*} Pierre-Louis Taberna,^b Patrice Simon,^{b,*} and Jean-Marie Tarascon^a

^aLRCS-UMR 6007, Université de Picardie Jules Verne, 80039 Amiens Cedex, France ^bCIRIMAT-UMR 5085, Université Paul Sabatier, 31062 Toulouse Cedex 4, France

We report that nanometric bismuth can directly be electrodeposited at room temperature without the use of a nanoporous template. The morphology, microstructure, and purity of the as-prepared electrodeposits were characterized by scanning electron microscopy, transmission electron microscopy, and infrared spectroscopy. Typically, well-crystallized nanometer-sized particles of Bi ranging from 10 to 20 nm are obtained. The key to success of such a process lies in the electrochemical coreduction of pyrocatechol violet during the bismuth deposition, which disturbs the electrocrystallization process. As a first possible application, we show that Bi/Cu nanoarchitectured electrodes exhibit interesting rate capabilities when used as electrode material vs Li. DOI: 10.1149/1.2826705

Bismuth, with a rhombohedral structure, has been widely studied for years because it exhibits interesting physical properties, including large magnetoresistance (MR) effects,¹ thermoelectric efficiency⁷⁻¹⁰ as well as large X-ray absorption making possible the elaboration of a highly sensitive X-ray imaging sensor.¹¹ In the field of electrochemical devices, beyond its electrochromic properties,^{12,13} Bi has been known for a long time to react with lithium following an alloying process at relatively low potential (i.e., near 0.8 V vs Li^+/Li^0).¹⁴⁻¹⁶ During the reduction step, LiBi and Li₃Bi alloys are formed leading to a pretty high volumetric capacity value of 3765 Ah L⁻¹ and a specific capacity value of 385 Ah kg⁻¹ (exceeding slightly that of graphite), making this semimetal somewhat attractive as negative electrode in a Li-ion battery. Nevertheless, little work has been reported in the literature because the electrochemical performances of such an electrode are still poor. Crosnier et al.¹⁷ and Brousse et al.¹⁸ have, however, pointed out that nanometric bismuth led to better electrochemical properties. Besides the field of electrochemistry, physicists have also shown (experimentally and theoretically) the benefits that nanosized Bi particles could have in improving MR effects as well as thermoelectric efficiency.²⁻¹⁰ Consequently, there is great potential interest in developing synthesis approaches for production of Bi nanoparticles particularly from soft chemistry routes because numerous applications can be envisioned.

A common approach to prepare powder of nanometer-sized bismuth from solutions involves an inversion micelle technique in the presence of additives to protect nanoparticles against aggregation.¹⁹⁻²¹ Electrochemical deposition has also become a well-developed technique for the elaboration of "nanometric Bi deposits." However, to date, direct electroplating of nanosized Bi has never been reported because its deposition usually leads to a dendritic growth of large particles. To overcome this drawback, Yang et al.^{2,3} have used the template-assisted synthesis process, previously developed by Martin,^{22,23} to produce arrays of electrodeposited Bi nanowires. The template method is a general approach that consists in growing the desired material onto a planar current collector using a nanoporous membrane acting as a template. Although quite reliable and highly attractive, this method cannot be operated in confining areas where the positioning of the physical membrane is made difficult or impossible. However, to preserve the positive attributes of electrodeposition techniques, namely, in their cost-effectiveness, simplicity, and applicability to shapeless surfaces, finding direct template-free electrodeposition approaches remains an interesting challenge.

In this preliminary communication, we report that thin films of nanometric bismuth can directly be prepared at room temperature by one-step electrodeposition onto a flat substrate as well as into the recesses of a surface. The concept is based on the electrochemical coreduction of soluble Bi(III) and of an electroactive cumbersome organic molecule, which interferes with the Bi deposition. This easy approach is somewhat similar to a recent electrodeposition strategy developed by Shin and Liu²⁴ to produce a three-dimensional copper nanostructure; the latter is based on the coreduction of cupric ions and protons from sulfuric acid baths. In Liu's process, the concomitant hydrogen evolution during the Cu plating limits the metal expansion and disturbs the mass transport conditions that lead to fabrication of a well-defined porosity through the copper film. Among the numerous molecules having a potential interest, pyrocatechol violet [(PCV), $C_{19}H_{14}O_7S$] has been selected for several reasons. In addition to be reducible,²⁵ PCV is also known to show a strong chelating effect toward the Bi^{3+} ion, thus preventing any precipitation reaction and facilitating the tenability of bath composition. Finally, as a first possible interest, Bi electrodeposits has been evaluated electrochemically vs Li in terms of rate capability from a selfsupported Bi/Cu nanoarchitectured electrode, copper being an efficient current collector in the field of Li-ion batteries.

Experimental

The electrochemical deposition of Bi films was conducted in a freshly prepared bath consisting of 0.01 M bismuth acetate (Alfa Aesar), 0.02 M pyrocatechol violet (Alfa Aesar) added to 5 \times 10⁻⁴ M sulfuric acid (Aldrich) to adjust the pH value to 3. By complexing with PCV, the bismuth is readily stabilized and the pH can be raised to moderate acidic values. The bath temperature was kept constant at 25 ± 0.1 °C during deposition by a Julabo FP 50 circulator. The substrate acting as the working electrode was either a conventional flat copper disk ($S = 2.01 \text{ cm}^2$) or a Cu nanoarchitectured current collector. The latter, elaborated according to a $\frac{27}{27}$ template-assisted electrochemical synthesis reported elsewhere, was composed of arrays of highly perpendicular copper nanopillars grown onto a copper disk ($S = 1.77 \text{ cm}^2$). A copper wire was wrapped around the edge of copper substrates to make electrical contact and maintain a horizontal position. Prior to the experiments, the flat copper disks were carefully polished and then successively rinsed with water, ethanol, and acetone before drying. Facing the working electrode, a large platinum coil was used as the counter electrode, whereas all potentials were quoted vs the mercuric sulfate reference electrode [(MSE), $E_{eq} = 0.64$ V/NHE]. Depositions and electrochemical investigations were conducted with an Autolab PG-STAT 30 potentiostat (Eco Chemie BV) without any magnetic stirring of the electrolyte baths. Additionally, it is worth noting that each plating bath was first purged with nitrogen for 5 h and subse-



Figure 1. Typical linear voltammograms recorded from a copper disk microelectrode for 0.02 M pyrocatechol violet without (a) and in the presence of 0.01 M bismuth acetate (b). Scan rate: 10 mV s⁻¹.

quently maintained under gas flux during deposition. Electrodeposits were examined by X-ray diffraction (XRD) measurements (Bruker D8 diffractometer), scanning electron microscopy (FEI QUANTA 200F), infrared (IR) spectroscopy (Nicolet AVATAR 370 DTGS), high-resolution transmission electron microscopy [(TEM), FEI TECNAI F20 S-TWIN] and energy-dispersive spectroscopy. Determination of the deposited mass of Bi was obtained by atomic absorption spectroscopy (Perkin Elmer Analyst 300, $\lambda_{Bi} = 223.1$ nm) after chemical leaching with 1 M HNO₃ of the Bi films deposited onto copper substrates. The measurements of electrochemical properties vs Li were performed with coin cell hardware, using the copper substrate covered with the Bi deposit directly, as positive electrode, Li-metal as negative electrode, and a fiberglass separator soaked with a molar LiTriflate solution (in ethylene carbonate dimethyl carbonate/1:1 in mass ratio) as the electrolyte. The cells were assembled in an argon-filled glove box and cycled using a versatile multipotentiostat potentiostat/galvanostat (Princeton Applied Research) operating in a galvanostatic mode and with a potential ranging between 1.5 and 0.3 V vs Li⁺/Li⁰.



Figure 2. SEM images of a deposit obtained for a fixed electrolysis time of 600 s. Inset: Higher magnification $(80,000 \times)$.

Results and Discussion

In order to find the suitable bismuth deposition conditions as well as to check the electrochemical activity of the PCV molecule, a conventional voltammetric study has been performed prior to any electrochemical deposition. Two cathodic scans have been performed from typical baths containing the PCV additive, without (Fig. 1a) and with (Fig. 1b) the presence of bismuth acetate. The main difference between these two voltammograms lies in the appearance at $E \approx -0.76$ V/MSE of a supplementary cathodic peak that can be ascribed to the Bi plating, the other being obviously linked to the reduction peak of the free PCV molecule. As expected, the two reduction steps are typical of diffusion-controlled processes.

In light of such observed electrochemical behavior, it should be possible to tune the Bi growth by taking advantage of the Bi(III)/PCV concomitant reduction. To do so, several deposits have been galvanostatically produced onto regular flat copper disks at relatively high current density (i.e., $j = -1.5 \text{ mA cm}^{-2}$) to force the PCV reduction. Figure 2 shows a typical scanning electron microscopy (SEM) picture of an as-deposited film obtained after an electrolysis time of 600 s. Interestingly, it can be found that the surface morphology consists of nanometric round-shaped particles uniformly distributed on the substrate, which is clearly different from the branchlike shape morphologies conventionally obtained in strong acidic baths (with or without complexing agents).²⁸

The deposits were amorphous at least with respect to X-rays since the collected XRD patterns were featureless. To further investigate the true texture, the crystallinity and structure of the electrodeposits as well as the elemental composition, a complete TEM study coupled with energy-dispersive spectroscopy (EDS) measurements have been performed. High-resolution TEM images realized on particles clearly show that the electrodeposits consist of small (from 10 to 20 nm) and well-crystallized particles (Fig. 3a) made of pure bismuth according to EDS analyses. The indexing of both the corresponding high Fourier transform resolution image (Fig. 3b) and selected area electron diffraction pattern (inset of Fig. 3c), realized on an agglomerate of particles, unambiguously indicates that the nanoparticles are Bi ones crystallizing in a rhombohedral unit characteristic of elemental Bi. Moreover, the absence of the characteristic peaks of sulphur on the EDS spectra shows that the deposit contains no trace of the PCV dye (i.e., this organic molecule having a sulfonate group). However, to further address this eventual contamination issue, a complementary IR investigation has been performed. Two pellets have been prepared by thoroughly mixing either the PCV dye or Bi powders recovered from the deposits with 100 mg of spectroscopic-grade potassium bromide (1 w/w %). Figure 4 shows the corresponding IR spectra recorded in transmission







Figure 3. TEM observation of electrodeposited particles (a) high-resolution TEM image, (b) corresponding fast Fourier transform with indexed spots, (c) treated selected area electron diffraction pattern (in inset) to obtain XRD-like diagram indexed with main rhombohedral bismuth phase reflections.



Figure 4. Infrared spectra recorded in transmission mode of both the dye molecule and powder of Bi deposits. For a better comparison, the two spectra have been shifted at the same scale.

mode. None of the characteristic bond vibrations of the dye molecule (or any other classical bond vibrations of organic molecules) is observed for the Bi-based sample, confirming that it is PCV free.

The as-produced Bi has then been electrochemically characterized vs Li. To promote better current collector/active material surface contacts as well as to better accommodate the structural change imposed by the electrode alloying reaction (i.e., volume increasing by a factor of 2.15 from Bi to Li₃Bi), nanometric bismuth has directly been electrodeposited onto a nanoarchitectured copper substrate easily homemade by a template-assisted synthesis method that we have recently developed.²⁷ This substrate consists of 200 nm diam and ~1.8 µm high copper nanorods evenly spaced on top of a copper foil. Since Martin's studies,^{22,23,29,30} it is now recognized that such nanostructured electrodes constitute a supplementary gain to promote the nanometric design compared to a conventional planar substrate especially in terms of diffusion length and reacting surface area as recently demonstrated with the Ni₃Sn₄ intermetallic compound during its Li alloying/dealloying process.³¹

The electrochemical growth of Bi onto these copper current collectors has been performed with a cathodic current density of -1.5 mA cm⁻², taking into account the geometrical surface area of the copper substrate ($S = 1.77 \text{ cm}^2$). Compared to the Cu planar substrate, we experienced that a slight mechanical stirring at 200 rpm is required to ensure a sufficient level of electrolyte inside the current collector nanoporosity so as to limit the Bi(III) concentration gradients, and by the same token to avoid the preferential growth on the top of Cu nanopillars. Figure 5 shows SEM images of the resulting self-supported Bi/Cu nanoarchitectured electrode after a deposition time of 1200 s (i.e., Q = 3.18 C). As expected, a highquality array of Bi/Cu nanorods is obtained displaying a perfect Bi distribution at nanoscale. Closer observations of the nanorods surface indicate that the Bi deposit is composed of very thin plateletshaped nanoparticles with a homogeneous degree of coverage along the nanorods. Because copper does not interfere with bismuth, the deposited mass was evaluated by atomic absorption spectroscopy after a complete Bi oxidation with nitric acid. The analytical measurements give an average value of 0.9 ± 0.04 mg. Knowing the mass and the charge passed (Q_{dep}) , the coulombic efficiency of the electrodeposit was evaluated at 40%, which confirms the PCV reduction as the dominant process in the overall cathodic reaction. Note that the water reduction does not take place prior to -1.6 V vs MSE.



Figure 5. SEM images (tilted and top views) of the resulting self-supported Bi/Cu nanoarchitectured electrode for a fixed electrolysis time of 1200 s.

Finally, the rate capability of our Bi/Cu nanoarchitectured electrodes has been investigated according to the protocol commonly used in the battery community.³² In short, after a first discharge recorded at a low current value (i.e., 1 Li⁺ exchanged per 5 h) to 0.3 V, a series of increasing current values has been applied to the cell for the subsequent charge using a cutoff potential of 1.5 V (Fig. 6). From the charge passed at each charge current value, a "signature curve" has been plotted and expressed, as required, in terms of C (Fig. 6, inset). A C rate is defined as the full use of the electrode capacity in 1 h. A detailed procedure can be found elsewhere.^{27,33} The relatively flat profile of the signature curve until an 8 C rate stresses the spectacular rate capability of this Bi-based electrode. Note that the cell can also recover 50% of its total capacity at a 64 C rate. Compared to a planar deposit of nanometric Bi (elaborated at $j = -1.5 \text{ mA cm}^{-2}$, t = 700 s, $m_{\text{Bi}} = 0.16 \text{ mg}$), the Bi/Cu nanoarchitectured electrode increases the energy density by a factor of \sim 12. Such staggering results are similar to what has been reported for other electrochemically active nanoarchitectured electrodes;^{27,29,31} they are nested in the high electrode surface area and its relative mechanical stability, which enable good electronic and ionic contacts owing to the shortening of the distance over which Li⁺ must diffuse in the solid.

Coming back to the first discharge profile, we should note that there is an extra capacity prior to reaching the two flat plateaus corresponding to the LiBi then Li_3Bi formation.^{14,15} Preliminary results have demonstrated that such an unexpected phenomenon is quite similar to the one already observed with tin-based electrodeposits and referred to as the high-voltage irreversible capacity.^{34,35} Its origin seems also to be nested in the catalytic activity of the freshly deposited metallic nanoparticles toward the electrolyte degradation. As a consequence, the electrochemical performances of such a cell upon cycling are affected especially at low rate. Figure 6



Figure 6. (a) Potential-composition curve for the Bi/Cu nanoarchitectured electrode. The discharge curve has been recorded at a rate of 1 Li⁺ exchanged per 5 h to 0.3 V, whereas a series of 12 decreasing current values has been applied to the cell during the subsequent charge up to 1.5 V (i.e., from 64 C till C/32 rate). Inset: The corresponding "signature curve" is plotted as the normalized capacity (mAh cm⁻² of plane surface area) vs rate. For comparison, the equivalent plot for a thin film of nanometric Bi deposited onto planar Cu is added. (b) Capacity-retention plot for a Bi/Cu nanoarchitectured electrode cycled at low rate (i.e., 1 Li⁺/10 h).

shows the corresponding capacity retention curve at a rate of one Li⁺ exchanged in 10 h. After five cycles one can observe a rapid decay reaching a stable value ~ 140 mAh g⁻¹. To suppress this effect and to maintain the original capacity retention, several tests regarding the electrolyte formulation are currently under progress.

Conclusions

In conclusion, we have succeeded in electrochemically depositing pure Bi nanoparticles directly from an aqueous solution at room temperature while a dendritic growth of large particles has thus far been reported under such conditions. Our innovation is based on the disturbance of the Bi electrocrystallization step by the coreduction of the PCV dye initially added to the electrolyte bath that produces PCV-free Bi nanoparticles. Typically, the morphology of the asobtained flat deposits consists of round-shaped particles with a constant crystallite size ranging from 10 to 20 nm. The rate capability of nanometer-sized Bi particles electrochemically grown on a selfsupported Bi/Cu nanoarchitectured electrode was strikingly high, exceeding 8 C without any capacity decay. Preliminary thermoelectric measurements of our films are also currently in progress. Lastly, this original electrochemical technique may lead to a new route for direct fabrication of other nanometer-sized metallic particles.

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