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Preparation of Manganese Thin Film in Room-Temperature Butylmethylpyrrolidinium Bis(trifluoromethylsulfonyl)imide Ionic Liquid and Its Application for Supercapacitors

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The butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-NTf₂) ionic liquid was found to have a very wide potential window of 4.5 V, making it capable of being a medium for electrodepositing metallic Mn thin film. By using an electrochemical process, block manganese counter electrode was dissolved in the ionic liquid to generate divalent Mn, which was subsequently cathodically deposited on the nickel substrate. The current efficiency of this process was confirmed to be extremely high (close to 100%). The Mn thin film can be oxidized to manganese oxide by cyclic voltammetry in Na₂SO₄ electrolyte. The obtained manganese oxide exhibited an excellent pseudo-capacitive performance and possessed a satisfactory specific capacitance of 265 F/g at a moderate cyclic voltammetric sweep rate of 25 mV/s.

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Electrochemical supercapacitors are charge-storage devices with greater power density and longer cycle life than batteries, and they possess higher energy density compared to conventional capacitors.¹ They have attracted much attention in many fields such as hybrid power sources, peak-power sources, backup-power storage, light-weight electronic fuses, and starting power of fuel cells, etc.^{2,3} The literature^{4,5} has reported that pseudo-capacitance of amorphous hydrous ruthenium oxide arises from the fast, reversible faradaic redox reaction that occurs near an electrode surface was higher than 700 F/g. Although excellent supercapacitive performance of the oxide was demonstrated, the high cost has limited its commercial applications. Manganese oxide, which is naturally abundant and much cheaper than ruthenium oxide, was also found to possess pseudo-capacitive characteristics. Therefore, it was considered to be the most promising novel electrode material for supercapacitors. Recently, various kinds of processes, including thermal decomposition,⁶ co-precipitation,⁷ sol-gel process,⁸⁻¹⁰ physical vapor deposition,¹¹ and anodic deposition,^{12,13} etc., have been developed to prepare manganese oxide with this demanding electrochemical property. It was confirmed that the preparation methods and/or conditions significantly affected the material characteristics of the manganese oxides, and, consequently, their corresponding pseudo-capacitive behavior. Therefore, searching for a more favorable fabrication process is worthy of further investigations.

Broughton et al.¹⁴ have demonstrated that manganese oxide with excellent pseudo-capacitive performance can be prepared by anodically oxidizing a metallic manganese thin film created by physical vapor deposition (PVD). The literature indicates that transformation of manganese oxide from its metallic state may be a feasible route to produce supercapacitor electrodes with higher performance. As compared to the PVD process, electrodeposition is a more convenient and cheaper method to produce metallic thin film. Moreover, the morphology, grain size, chemical state, and thickness of the deposit can be easily controlled by varying the electrochemical parameters such as potential, current density, bath composition, and temperature. An optimum Mn thin-film electrode for the supercapacitor application, therefore, could be achieved by electrodeposition. However, because the reduction potential of Mn is lower than that of hydrogen, electrodeposition of Mn in aqueous solution is very difficult to control due to serious hydrogen evolution. Aprotic room-temperature ionic liquids owing to their proton free character-

istics have been successfully proposed by Endres et al.¹⁵⁻¹⁷ to electrodeposit highly active metals such as Al, Ta, and Si, etc. Nevertheless, preparation of metallic Mn in ionic liquid is still a challenge and was rarely reported in the literature,¹⁸ hence we attempted to study its practicability in BMP-NTf₂ ionic liquid in this investigation. Although electrochemical oxidation of bulk transition metals was discussed by Trasatti,¹⁹ herein we propose the oxidation behavior of the nanocrystalline Mn thin film with special surface morphology which was electrodeposited in the BMP-NTf₂ ionic liquid. Application of the oxide electrode in a supercapacitor was also evaluated.

Experimental

The BMP-NTf₂ ionic liquid was prepared and purified principally according to the method described in the literature.²⁰ The ionic liquid was transferred to a nitrogen-filled glove box and then eliminated trace water by an electrolysis process. Cyclic voltammetric (CV) behavior of a glassy carbon electrode was measured in this solution. A Pt wire was used as the counter electrode. The reference electrode was a Pt wire placed in a separated fritted glass tube containing BMP-NTf₂ ionic liquid with the ferrocene/ferrocenium couple [Fc/Fc⁺, +0.55 V vs a standard hydrogen electrode (SHE)] as the internal reference standard. Afterward, manganese ion was introduced into the ionic liquid by anodically oxidizing a manganese block (Alfa Aesar, 99.9%) to 0.05 M. A sufficient positive potential of 0.5 V (vs Fc/Fc⁺ couple) was applied on the manganese block, and a Pt wire was used as a counter electrode. To prevent undesired impurity created during the process from polluting the ionic liquid, the Pt counter electrode was separated in a glass tube with a porous ceramic tip.

Manganese thin films were fabricated by cathodic deposition in the above-mentioned ionic liquid at 50°C. The electrochemical deposition was accomplished with an Autolab potentiostat/galvanostat controlled by GPES software. A three-electrode electrochemical cell was adopted for the experiment. Nickel foil (with 1 cm² area and ~120 μm thick) was etched in an 85°C 1 M H₂SO₄ solution, then washed with pure water in an ultrasonic bath, and finally used as the working electrode. The reference electrode was the same as previously described. In addition, the counter electrode was a manganese block, which can compensate the consumption of manganese ion in the ionic liquid during the electrochemical deposition process. The deposited manganese was dissolved by 2 M nitric acid, and the amount was determined by an atomic absorption spectroscope (AAS, SOLAAR M6).

The electrochemical property of the manganese thin film was

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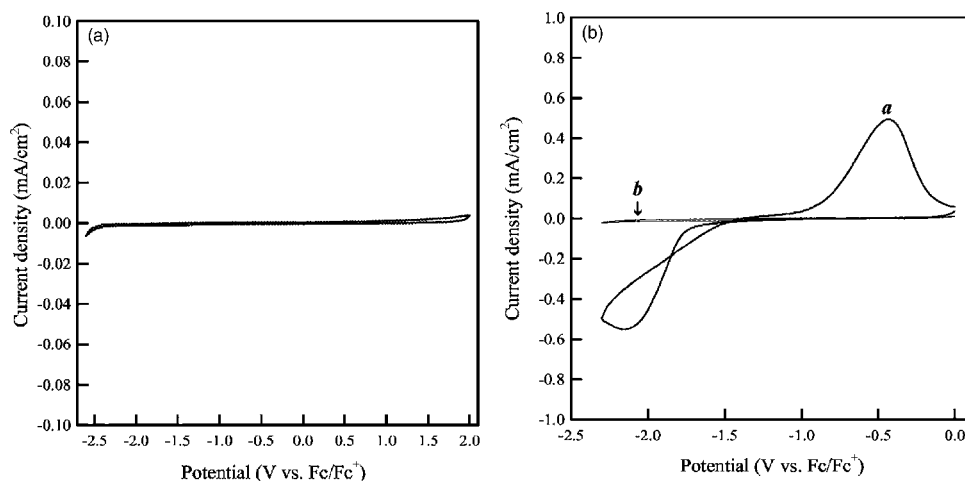


Figure 1. (a) Voltammogram of a glassy carbon electrode in the pure BMP-NTf₂ ionic liquid. (b) Voltammetric response of nickel substrates in the Mn(II) contained BMP-NTf₂ ionic liquid (curve a) and the pure BMP-NTf₂ ionic liquid (curve b).

examined by CV in 0.1 M Na₂SO₄ aqueous solution at 25°C. The counter and reference electrodes were a platinum sheet and a saturated calomel electrode (SCE), respectively. An EG&G M263 was used to perform the test in the range of 0–0.9 V (vs SCE) with a sweep rate of 25 mV/s. Surface morphologies of the deposited manganese thin films before and after the CV experiment were observed using a scanning electron microscope (SEM, Philip XL-40FEG). An auxiliary X-ray energy dispersive spectroscope (EDS) was also carried out to examine the chemical composition. Pseudocapacitive performance of the prepared oxide was evaluated by chronopotentiometry (CP) with an applied current of 0.5 mA.

Results and Discussion

To explore the electrochemical potential window of the pure BMP-NTf₂ ionic liquid, CV behavior of an inert glassy carbon electrode was measured in this solution. The voltammogram determined at a potential sweep rate of 50 mV/s is shown in Fig. 1a. The result indicated that the ionic liquid possessed a very wide potential window stretching from –2.5 to 2 V (vs Fc/Fc⁺ couple). Within the potential range the ionic liquid was considered to be stable, and no redox reaction occurred, suggesting it could be a promising solvent for electrodepositing very reactive elements. Manganese cations were thereafter introduced into the ionic liquid by anodic dissolution of a manganese block. For understanding the number of charges carried by the Mn cations which were produced by anodic dissolution, the weight change of the manganese block was measured after passing a given amount of anodic charge. The data collected during several controlled-potential coulometry experiments (not shown here) revealed that the calculated number of electrons transferred during the anodic dissolution of manganese were all in the range of 1.99–2.02. Clearly, divalent manganese cations were the anodized products existing in the BMP-NTf₂ ionic liquid.

The Mn(II) contained BMP-NTf₂ ionic liquid was used to perform electrochemical deposition of manganese at 50°C. The working electrode in this experiment was a nickel substrate. Curve a in Fig. 1b represents the voltammetric response of this electrochemical system in which the potential was initially swept to negative (cathodic) direction. Apparently, Mn(II) in the ionic liquid can be reduced to its metal state at a sufficiently negative potential, beginning at around –1.75 V (vs Fc/Fc⁺ couple). In addition, an obvious cathodic current loop occurred during the reverse sweep indicating that the nucleation process happened during the cathodic deposition of manganese. This nucleation mechanism usually happens along with the electrodeposition of metals on foreign substrates. A corresponding anodic peak, located at about –0.43 V, was also observed. The result revealed that the deposited manganese solid film was dissolved during the subsequent anodic sweep. However, it was found that the total charges integrated from the cathodic region were 60% higher than those of the anodic region. The fact pointed out that

only a certain portion of Mn deposit could be oxidized after it had been formed. Mn (II) needed Tf₂N[–] anions to form complex ions to be dissolved in the ionic liquid. This process may be too slow to respond to the high potential scan rate (50 mV/s), and consequently resulted in the partial dissolution of Mn. The voltammogram of an identical nickel substrate in the pure BMP-NTf₂ ionic liquid without Mn (II) was also superimposed as curve b in this figure. The comparison result indicated that the nickel electrode was inert in this potential range and was capable of being a suitable substrate.

In aqueous solution, the major problem encountered in electrodeposition of manganese is the very low current efficiency, resulting from the serious hydrogen evolution. The formation of hydrogen gas during deposition would also cause the reduction in uniformity and density of the deposit. It is very difficult to prevent hydrogen formation because the reduction potential of manganese is much more negative than that of hydrogen evolution. However, as discussed in the previous paragraph, the reduction potential of Mn (II) in the aprotic ionic liquid (–1.75 V) is still far away from the cathodic limit (–2.5 V) of the electrochemical window. Therefore, it is expected that the Mn deposition efficiency in this ionic liquid could be high. In this study, the deposition current efficiency was evaluated by measuring the amount of Mn deposit and comparing with the theoretical value (the deposition reaction of Mn²⁺ + 2e[–] → Mn was assumed). Manganese was cathodically deposited on the nickel substrates by a constant potential of –1.8 V (vs Fc/Fc⁺ couple) to 0.2, 0.3, 0.4, and 0.5 Coulomb, respectively. Then, the deposits were totally dissolved in 2 M HNO₃ solution, and the amount of Mn was analyzed by an atomic absorption spectroscope (AAS, SOLAAR M6). The experimental results are summarized and listed in Table I. The deposition efficiencies were all higher than 96%, and even very close to 100% in some cases. As expected, the extremely high current efficiency demonstrated that the BMP-NTf₂ ionic liquid is a promising solvent for electrodeposition of manganese. Also included

Table I. Deposition time and current efficiency of preparing various amounts of manganese, which were controlled by total cathodic charge applied.

Deposition charge	Deposition time	Theoretical mass of Mn (μg)	Experimental mass of Mn ^a (μg)	Efficiency (%)
0.2	770	56.93	55.79	98
0.3	1150	85.40	84.89	99
0.4	1610	113.87	109.31	96
0.5	2000	142.33	141.34	99

^a The data are measured by an atomic absorption spectroscope (SOLAAR M6).

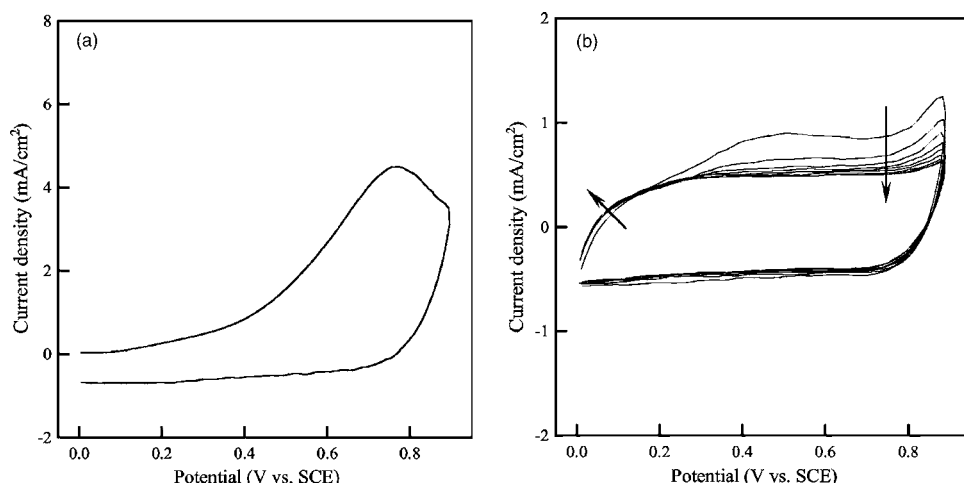


Figure 2. CVs of the manganese thin film in 25°C 1 M Na₂SO₄ aqueous solution. (a) The first cycle and (b) the subsequent 2–10 cycles. The potential sweep rate is 25 mV/s.

in Table I are the deposition times for different Mn quantities, indicating the deposition rate was almost constant (4.3 μg/min).

Accordingly, a novel and promising process to prepare manganese thin films was successfully proposed in this study. The BMP-NTf₂ ionic liquid worked only as an inert medium or solvent, which was not consumed during the process and could be reusable. Free of waste disposing problem has made it an environmentally friendly scheme, and wide range potential applications could be expected. Moreover, the significant advantage of this Mn thin film preparation process is the ease of electrochemically controlling the deposition rate and thickness by adjusting potential and total pass charge, respectively. Moreover, the roughness and morphology of the thin film were also found to substantially change with the electrodeposition conditions. Further investigation is already underway and will be published elsewhere. Actually, the mechanism of this wet electrochemical deposition process is very similar to that of the PVD process, which is a common method to prepare Mn thin films.¹¹ The manganese block was consumed at the counter electrode (like the target in the PVD system) and deposition on the desired substrate. Note, however, that the PVD process requires much more complicated and expensive equipment as compared to the electrochemical method. The yielding rate of the PVD process is also much lower. Most importantly, the conversion efficiency (Mn from the target to substrate) for PVD is low, because most Mn is deposited on the chamber wall. On the contrary, almost 100% efficiency can be obtained as the electrochemical deposition of manganese was performed in the BMP-NTf₂ ionic liquid.

The electrochemical property of the manganese thin film, deposited at -1.8 V (vs Fc/Fc⁺ couple) for the total pass charge of 0.3 C, was examined by CV in 0.1 M Na₂SO₄ aqueous solution. Figure 2a shows its typical first-cycle voltammogram with a potential sweep rate of 25 mV/s. A very broad and irreversible anodic peak was observed. The result indicated that the Mn metallic thin film was oxidized in the electrolyte. According to the Pourbaix diagram,²¹

Mn could be electrochemically transferred to Mn²⁺, Mn₃O₄, Mn₂O₃, and MnO₂ with increasing the anodic potential in this neutral aqueous solution. The subsequent CV cycles of the electrode were superimposed in Fig. 2b. Although the further oxidation reaction was still visible, the electrochemical behavior of the electrode gradually became stable. After ten cycles of CV sweep, a fully anodized manganese oxide was formed and the electrode demonstrated a steady capacitor-like behavior. The final CV curve was close to rectangular shapes and exhibited mirror-image characteristics, suggesting its excellent reversibility and ideal pseudo-capacitive property. The fully anodized manganese oxide was dissolved in 2 M HNO₃ solution and the amount of Mn was quantified by AAS. The Mn concentration in the Na₂SO₄ testing solution was also analyzed in the same manner. The analytical data revealed that about 40 (±5)% of the original manganese was dissolved into Na₂SO₄ electrolyte (to form Mn²⁺) during the CV cycling, while the 60 (±5)% remained on the substrate and anodically transferred to manganese oxide. Djurfors et al.²² had reported that Mn₃O₄ was formed as the metallic Mn was electrochemically oxidized in Na₂SO₄ electrolyte. Assumed that the electrochemical active material was Mn₃O₄ and took account of the 40% originally deposited Mn dissolution, the specific capacitance of the oxide was as high as 265 F/g measured at a CV sweep rate of 25 mV/s. Calculation of oxide capacitance from the CV curve followed the method described previously.¹³ This satisfactory capacity is at least 40% higher than that of the manganese oxide prepared by anodic deposition (based on the same testing condition), as reported in our previous study.¹³

Figures 3a and b show the SEM surface morphologies of the deposited manganese thin films before and after the CV oxidation process. The as-deposited Mn film was composed of spherical particles with the diameter of ~400 nm. However, close examination further revealed that each particle consisted of numerous sub-grains with a few nanometers in the size. After the oxidation process, the

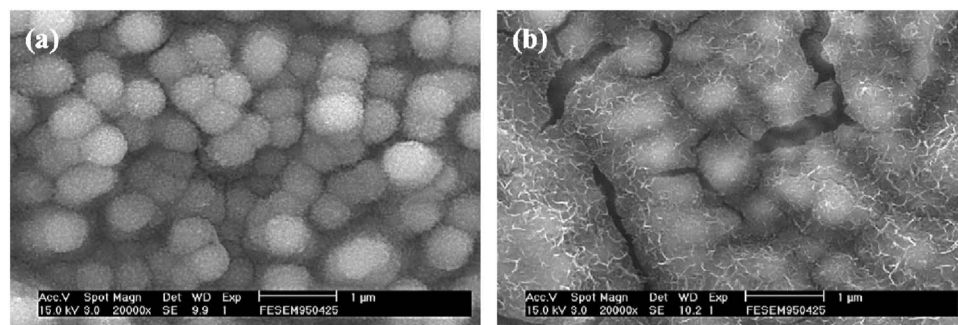


Figure 3. Surface morphologies of the electrochemically deposited manganese thin film (a) before and (b) after the oxidation process.

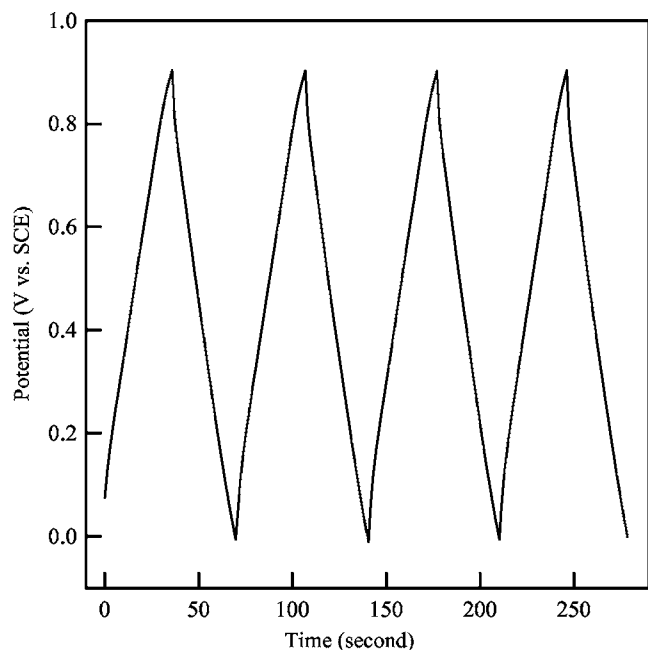


Figure 4. Chronopotentiogram of the manganese oxide electrode measured in 0.1 M Na_2SO_4 electrolyte with an applied current of 0.5 mA.

particles were found to lump together as shown in Fig. 3b, due to the volume expansion of oxide formation. Moreover, the fiberlike microstructure, which is typical for the anodically deposited manganese oxide^{23,24} was also clearly observed on the surface. The cracks recognized in this figure were suggested to have been caused by shrinkage stress during drying. Chemical composition analysis of the manganese oxide was also performed by EDS, and the Mn/O atomic ratio of 43/57 was found. The experimental data implied that the Mn metallic thin film could transform to Mn_3O_4 after the CV oxidation process. This result coincided well with the literature.²²

Galvanostatic charge-discharge performance of the fully anodized manganese oxide electrode was examined. Figure 4 shows its chronopotentiogram of initial four charge-discharge cycles in 0.1 M Na_2SO_4 electrolyte with an applied current of 0.5 mA. Good symmetry and near-linear slope in both charge and discharge branches again supported that the oxide electrode was electrochemically reversible and possessed excellent pseudo-capacitive characteristics. After 500 charge-discharge cycles, about 90% capacitance of the oxide electrode can be retained which was 10% higher than that of the anodically deposited manganese oxide reported in our previous paper.²⁵ The experimental result clearly revealed the great electrochemical stability of the manganese oxide prepared in this study.

Conclusions

A promising electrochemical deposition process was successfully proposed to prepare metallic manganese thin films in the room-

temperature BMP-NTf₂ ionic liquid. An extremely high current efficiency and an almost constant deposition rate would make the process very precise and easily controlled. The prepared Mn thin film can be anodized in Na_2SO_4 electrolyte and transformed to manganese oxide. The manganese oxide exhibited excellent pseudo-capacitive performance and provided the capacitance of 265 F/g at a moderate CV sweep rate of 25 mV/s. Moreover, ~90% of initial capacitance can be retained after 500 charge-discharge cycles. A further study to improve the oxide electrochemical property has been started and will be reported in the near future. Optimizations of the deposition and anodization conditions are attempted to control the film morphology and chemical state, which were considered to be the critical issues as pseudo-capacitive performance of the oxide was concerned.

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