Preparation of cobalt oxide on MXene/N, S-rGO surface for supercapacitors

G Threepiriyamongkol\(^1\) and P Pattananuwat\(^2,3,\,*\)

\(^1\)Department of Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand
\(^2\)Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand
\(^3\)Research Unit of Advanced Materials for Energy Storage, Chulalongkorn University, Bangkok, Thailand

E-mail: *prasit.pat@chula.ac.th

Abstract. The electrodeposited cobalt oxide grown on MXene/N, S-rGO surface was successfully synthesised via chronoamperometry technique at -1.2 V. The effect of MXene/N, S-rGO surface and electrodeposition time of cobalt oxide on the electrocapacitive behaviour was investigated. SEM-EDS evidenence confirmed that the highly dense growth of flake-like structure of cobalt oxide with interconnected pores was obtained on MXene/N, S-rGO surface. The synergistic effect of cobalt oxide grown on MXene/N, S-rGO surface can enhance the electrochemical properties with the highest specific capacitance of 608.3 F/g at 1 A/g (628.8 F/g at 10 mV/sec) with 35.7 Wh/kg and 180.6 kW/kg.

1. Introduction

Cobalt oxide is one of classic metal oxide applying for supercapacitors owning to its pseudocapacitor features. It can be easily synthesized in many techniques such as hydrothermal, sol-gel and electrodeposition technique, etc. Among of them, the electrodeposition technique is one of the most attractive attention methods because it can be deposited directly onto the substrate materials. This technique can be controlled the amount of cobalt oxide by the different deposited times. However, the limitation of electrodeposition technique is the lack of adhesion between the surface which depends on substrate types, causing the occurring of low yield of the deposited active materials. Thus, the modification surface of substrate is required to improve the surface activity. Several reports demonstrated that the using of materials coating, such as metal particle, carbon and so on, covering on the substrate can improve the surface adhesion. Recently, the discovery of the new electric storage materials, namely titanium carbide or MXene (Ti\(_3\)C\(_2\)Tx) possesses the 2D multilayer structure with a large surface area.

MXene has a theoretical hybrid capacitor attributing to redox reaction [1]. However, the restacking problem in its own morphological structure of MXene is reported, causing the loss of surface area for redox reaction [2]. Hence, the delamination of MXene layer is required to maintain 2D layer structure by adding organic solvent or small molecules such as dimethyl sulfoxide (DMSO) or carbon nanotubes (CNT) and graphene (rGO). The insertion of small molecules such rGO for intercalating between layer has been proved to exfoliate the self-restacking. In addition, the using of rGO doped...
nitrogen/sulfur atoms exhibited the beneficial features of more electron donor for enhancing the electrochemical performance [3]. Thus, in this work, the effect of MXene/N, S-rGO surface for the electrodeposited cobalt oxide growth is studied. The optimum condition for deposited time of cobalt oxide on MXene/N, S-rGO surface is also investigated to achieve the specific capacitance values.

2. Experimental section

2.1. Preparation of MXene/N, S-rGO coated materials on nickel foam
MXene was typically synthesized by etching of Al atom layers from the Ti$_3$AlC$_2$ precursors with HF, following by exfoliation process in dimethyl sulfoxide for 24 h. For graphene doped with nitrogen and sulfur atom, graphene oxide (GO) was synthesized by modified Hummer method [4]. GO was doped with nitrogen and sulfur atom, then partially reduced by reflux process in thiourea aqueous solution at equivalent weight, denoted as N, S-rGO. The obtained MXene and N, S-rGO were mixed at ratio of 95:5 in the aqueous solution under sonicate for 3 h. Subsequently, the mixture was dropped onto the nickel foam sheet and dry at 70 °C.

2.2. Preparation of cobalt oxide and cobalt oxide/MXene/N, S-rGO electrode samples
The cobalt oxide was electrochemically deposited from the solution of 0.05 M Co(NO$_3$)$_2$·6H$_2$O via chronopotentiometry technique at constant potential of -1.2 V. PGSTAT 12 equipped with a conventional three-electrode cell system consisting of MXene/N, S-rGO/nickel foam as working electrode, platinum as counter electrode and Ag/AgCl as reference electrode was used to employ the deposition process at various time of 60, 180 and 300 sec which are denoted as MxG-Co1, MxG-Co2 and MxG-Co3, respectively. The direct electrochemical deposition of cobalt oxide on the bare nickel foam substrate with similar process at 60, 180 and 300 sec, denoted as Co1, Co2 and Co3, respectively, was also done to compare the effect of MXene/N, S-rGO coated materials.

2.3. Characterization
The surface morphology and elemental analysis of samples were observed using field emission scanning electron microscopy (FE-SEM: JSM-7610F, JEOL) at an acceleration voltage of 15 keV. The samples were coated with 10 nm of gold before being observed.

2.4. Electrochemical measurements
The electrochemical properties of the as-prepared cobalt oxide/MXene/N, S-rGO electrode samples were examined in 6 KOH using three-electrode system configuring with platinum as electrode counter and Ag/AgCl as reference electrodes. PGSTAT 12 equipment was used for cyclic voltammetry (CV) measurements and galvanostatic charge/discharge (GCD). CV experiments were executed in the range of -0.3 to 0.45 V at different scan rates. The range of -0.2 to 0.40 V at different current densities was adjusted for measuring the GCD curves. The specific capacitance by CV was calculated according to the following equations [5].

\[
C_{sp} = \frac{\int I \, dV}{(2v \times m \Delta V)} \quad (1)
\]

Galvanostatic charge-discharge (GCD) measurement was carried out at various current densities. The specific capacitance by GCD was calculated according to the following equations [6].

\[
C_{sp} = \frac{I \Delta t}{(m \Delta V)} \quad (2)
\]

Where \(C_{sp} \) (F/g) is the specific capacitance, \(v \) (V/s) is the scan rate. \(I \) (A) is the discharge current. \(\Delta t \) (s) is the discharge time. \(m \) (g) is the mass of composite on substrate. And \(\Delta V \) (V) is the potential window without the hydrogen evolution.
3. Results and discussion

3.1. Morphology study

Figure 1a shows the SEM images of cobalt oxide on nickel foam at the deposition time of 180 sec, demonstrating the densely anisotropic growth of uniform flake structure derived from cobalt oxide. Obviously, the denser growth of flake-like structure of cobalt oxide with interconnected pores can be obtained from MXene/N, S-rGO surface for all the deposition times. The remarkable increase in dense flake-like structure with the increase deposition time is also presented for cobalt oxide deposited onto MXene/N, S-rGO surface. Some of aggregated cobalt oxide structure is found at the deposition time of 300 sec (Figure 1d). These evidences imply that the coated MXene/N, S-rGO possesses the beneficial feature for cobalt oxide deposition. Additional evidence from SEM-EDS reveals the existence of cobalt oxide, carbon and titanium on surface as seen in figure 1e, confirming coexistence of titanium carbide and cobalt oxide on surface electrode.

![SEM images](image)

Figure 1. SEM images of (a) Co2, (b) MxG-Co1, (c) MxG-Co2, (d) MxG-Co3, (e) EDS analysis of MxG-Co2.

3.2. Electrochemical properties

CV curves in figure 2a show the electrochemical activity of the cobalt oxide electrodes at different deposition times. Figure 2b shows the CV curves of the cobalt oxide on MXene/N, S-rGO surface at different deposition times. As seen in figure 2a and 2b, the remarkable redox peaks of cobalt oxide electrodes and cobalt oxide on MXene/N, S-rGO obviously reveal the different faradic characteristics. All of cobalt oxide on MXene/N, S-rGO exhibits the higher in CV area than that of cobalt oxide on nickel foam, indicating the higher electrochemical activity. This evidence confirms the good synergistic effect between the cobalt oxide and titanium carbide causing in increasing in pseudocapacitance behaviour.

The calculated specific capacitance values by CV for cobalt oxide and cobalt oxide onto MXene/N, S-rGO at the different deposition times are presented in figure 2c. It is clear that all cobalt oxide deposited onto MXene/N, S-rGO samples show the highly efficient electrochemical activity surface that of cobalt oxide deposited onto nickel foam. Among of MxG-Co series, MxG-Co2 can deliver the highest specific capacitive of 628.8 F/g. These results also correspond agreement with SEM results supporting that the high active surface of flake-like structure with interpore connection of MxG-Co2 can provide a facile shortcut path for charge transfer increasing a more efficient electrocapacitive properties. The slightly decrease of MxG-Co3 (489.7 F/g) is arisen from the aggregated cobalt oxide structure causing the decrease in charge transfer surface. The electrochemical performance of MxG-Co2 electrode at various scan rate is also evaluated as shown in figure 2d. A pair of redox peaks of samples was clearly observed for each curve and can be maintained, even at high scan rate. The good
rate capability of MxG-Co2 electrode with capacitance preservations is around 55% (from 628.8 to 346.4 F/g).

Figure 2. CV curves of (a) Co1, Co2 and Co3, (b) MxG-Co1, MxG-Co2 and MxG-Co3, (c) The calculated specific capacitance of samples, (d) CV curves of MxG-Co2 at various scan rates.

In addition, GCD curves in figure 3a show the charge-discharge profile of the cobalt oxide electrodes at different deposition time. Figure 3b shows the GCD curves of the cobalt oxide on MXene/N, S-rGO surface at different deposition time. All sample electrodes reveal the distinct pseudocapacitive characteristic with a presence of a large plateau in GCD curves. Among of electrode samples, MxG-Co2 reveals the longest plateau region for charge transfer reaction, indicating the highest capacitance. The specific capacitance (Cs) of cobalt oxide electrode samples calculated from discharge time at 1 A/g are displayed as figure 3c. The specific capacitance values at 1 A/g of Co1, Co2, Co3, MxG-Co1, MxG-Co2 and MxG-Co3 are 193.3, 365.83, 253.3 and 514.2, 608.3, 435.8 F/g, respectively. Figure 3d displays the good rate capability of MxG-Co2 with capacitance preservations of 57.5% (from 608.3 to 350 F/g) as the increasing of current density from 1 to 10 A/g, which is a good agreement with CV results.

Figure 3. GCD curves of (a) Co1, Co2 and Co3 (b) MxG-Co1, MxG-Co2 and MxG-Co3, (c) The calculated specific capacitance of samples, (d) GCD curves of MxG-Co2 at various current densities.
4. Conclusions
The electrodeposited cobalt oxide grown on MXene/N, S-rGO surface has been developed to increase electrochemical supercapacitor performance by the beneficial features of the synergistic effects from pseudocapacitor mechanism between cobalt oxide and MXene/N, S-rGO surface. The high active surface of flake-like structure with interpore connection of cobalt oxide surface of MxG-Co2 can deliver the highest specific capacitance of 608.3 F/g at 1 A/g (628.8 F/g at 10 mV/s) with energy density of 35.7 Wh/kg and power density of 180.6 kW/kg.

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