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Short communication

Ultra-high-rate all-solid pseudocapacitive electrochemical capacitors

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HIGHLIGHTS

- ► A solid redox supercapacitor with ultra-high rate performance was demonstrated.
- ► Mo_xN electrodes and a solid polymer electrolyte form thin/flexible supercapacitors.
- ► Due to redox reactions, a capacitance of 1 mF cm^{-2} was delivered at 100 Vs^{-1}.

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ABSTRACT

A solid pseudocapacitive electrochemical capacitor (EC) enabled by a polymer electrolyte and molybdenum nitride electrodes has been developed and has demonstrated ultra-high rate performance. The solid EC can deliver 1 mF cm^{-2} at 100 Vs^{-1} and achieve a 10 ms time constant. This not only exceeds its liquid EC counter-part but also greatly surpasses a similar EC with titanium nitride electrodes as well as nanocarbon based electrochemical double layer capacitors.

1. Introduction

Although electrochemical capacitors (EC) are high power energy storage devices, their application in the microelectronics industry has by far been limited due to their moderate charge–discharge rates compared to electrolytic capacitors as well as their large and bulky form factors. Only recently, ECs with ultra-high rate capability (up to 400 Vs^{-1} and 120 Hz filtering) have been reported [1–6]. ECs store energy via electrochemical double layer capacitance (EDLC) or via Faradic charge transfer reactions (also known as pseudocapacitance). While EDLC originates from the rapid adsorption/desorption of ions, pseudocapacitance involves slower electrochemical oxidation–reduction reactions but can store 10–100 times more charge than EDLC [7]. To date, ultra high-rate ECs are all based on EDLC utilizing advanced carbon nanomaterials such as onion-like nanocarbon [1] or graphene [2,3] in liquid electrolyte systems or using graphite in advanced polymer electrolytes [5,6]. These thin and highly conductive nanocarbon electrodes possess a readily accessible surface, which enables high rate performance. To further improve the energy density of ECs, metal-based pseudocapacitive electrodes could be exploited. High-rate pseudocapacitive ECs (also known as redox supercapacitors) so far have been limited to expensive RuO_2 electrodes [8,9]. Transition metal nitrides, such as V_xN, Mo_xN, and TiN, have been reported to possess pseudocapacitive properties, and could potentially become low-cost alternatives to RuO_2 [10–13]. To develop ECs with thin and flexible form factors and with multi-cell/single packaging, polymer electrolytes are key enablers since they can act, at the same time, as separators and ionic conductors without leakage issues. The most mature polymer electrolytes are Nafion® and its derivatives [14]. Although they have been reported as electrolytes for ECs [15,16], they are highly sensitive to humidity at ambient operating temperatures [14,17]. Heteropoly acids (HPAs) [18] are promising solid proton conductors. Excellent rate and stability have been demonstrated for two common HPAs, silicotungstic acid (SiWA, $H_4SiW_{12}O_{40}$) and phosphotungstic acid (PWA, $H_3PW_{12}O_{40}$), immobilized in a polyvinyl alcohol (PVA) matrix [5,6,17,19]. Based on a solid-polymer electrolyte composed of SiWA, PVA, and H_3PO_4 (henceforth referred to as SiWA–H_3PO_4–PVA), we have developed all-solid ECs reaching rates as high as 20 Vs^{-1} with graphite EDLC

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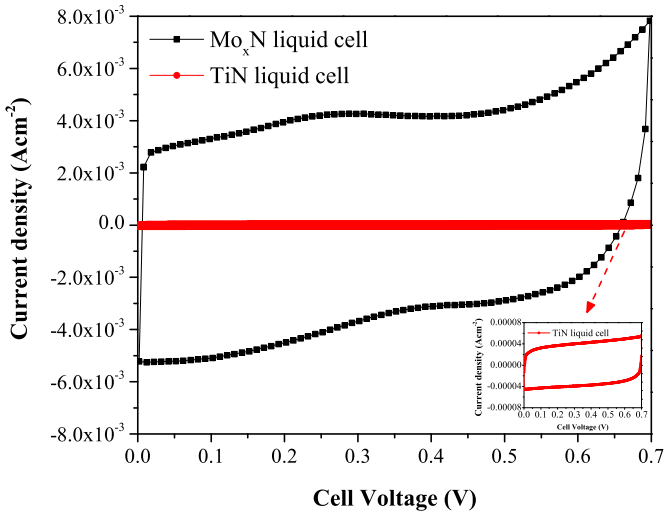

Fig. 1. CVs of liquid Mo_xN EC cell and liquid TiN EC cell (also shown as inset) with 0.5 M H_2SO_4 aqueous electrolyte at sweep rate of 1 Vs^{-1}.

electrodes [5]. Although these solid EDLC devices exhibited high-rate performance, their capacitance was relatively small. It is our objective to leverage metallic pseudocapacitive electrodes and a solid polymer electrolyte to develop ultra-high-rate, all-solid pseudocapacitive ECs. In this paper, we report a solid pseudocapacitive EC achieving 1 mF cm^{-2} cell capacitance at 100 Vs^{-1} with a 10 ms time constant. Due to pseudocapacitance, this is the highest area-specific capacitance at 100 Vs^{-1} reported to date for any EC device, liquid or solid.

2. Experimental

The SiWA–H_3PO_4–PVA polymer precursor solution was prepared by mixing a poly(vinyl alcohol) (PVA, Aldrich MW = 145,000) solution with SiWA ($H_4SiW_{12}O_{40}$, Alfa Aesar), and Phosphoric acid (H_3PO_4, Alfa Aesar) in a composition of 14.4% SiWA, 1.9% H_3PO_4, 1.7% PVA, and 82% de-ionized water (all in wt.%). The electrodes were either molybdenum nitride on a titanium substrate (Mo_xN) or nitrided titanium (TiN).

Mo_xN electrodes were prepared by nitridation of electroplated Molybdenum oxides. Electroplating of molybdenum oxide was carried out on the titanium substrate using a CHI 660 potentiostat, by sweeping an applied voltage from 0 to −0.75 V, cycling at a rate of 0.3 Vs^{-1}. In this 3-electrode plating system, the working electrode was titanium foil, the reference electrode was Ag/AgCl, and the counter electrode was a large area titanium sheet. The electroplating bath was prepared by dissolving $MoNaO_4 \cdot 2H_2O$ and Na_2SO_4 in de-ionized water to obtain a solution containing 0.4 M Na_2MoO_4 with a pH value of 2. Nitridation was carried out in a nitrogen atmosphere at 400 °C using a tube furnace. For the TiN electrodes, titanium foils (Grade 2, Trinity Industries Inc.) were heated in a nitrogen environment similar to the electroplated Mo samples.

Solid-state EC devices were then assembled as reported in previous studies [5,6]. The electrolyte precursor solution was first coated onto both sides of the identical electrodes and dried in air. The coated electrodes were then laminated, with the electrolyte sandwiched in the middle, at 10–12 psi and 90 °C for 15 min. The geometric area of the electrode was 0.8 cm^2 and the electrolyte thickness was in the range of 0.1–0.15 mm. For comparison, liquid EC devices utilizing a 0.15 mm thick filter paper soaked in a 0.5 M H_2SO_4 solution and sandwiched between the electrodes were also tested. The 0.5 M H_2SO_4 solution was selected to ensure the stability of Mo_xN. All EC devices were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using a CHI 760D bipotentiostat. All electrochemical characterizations were conducted at ambient temperature. Scanning electron microscopy (SEM) micrographs were obtained using a Hitachi S-570 to study the morphologies of the Mo_xN and TiN surfaces. The surface roughness and coating thickness of the electrodes were also examined on a Zygo New View-100 optical profilometer.

3. Results and discussion

The pseudocapacitive electrode was a molybdenum nitride (Mo_xN, $x = 1–2$) film coated on a titanium substrate. The coating thickness was less than 100 nm. Its electrochemical behavior was compared with the TiN electrode. Fig. 1 shows the CV of a Mo_xN EC overlaid with the CV of a TiN EC in a 0.5 M H_2SO_4 aqueous electrolyte. The Mo_xN EC device exhibited an area-specific capacitance of 4.5 mF cm^{-2} at 1 Vs^{-1}, about 100 times greater than that of the TiN EC (inset).

To understand the origin of the excess capacitance of the Mo_xN EC, the surface morphologies of TiN and Mo_xN electrodes were examined by scanning electron microscopy (SEM). As shown in Fig. 2, both TiN and Mo_xN electrodes have a similar surface roughness. In addition, both TiN and Mo_xN cells were tested in an

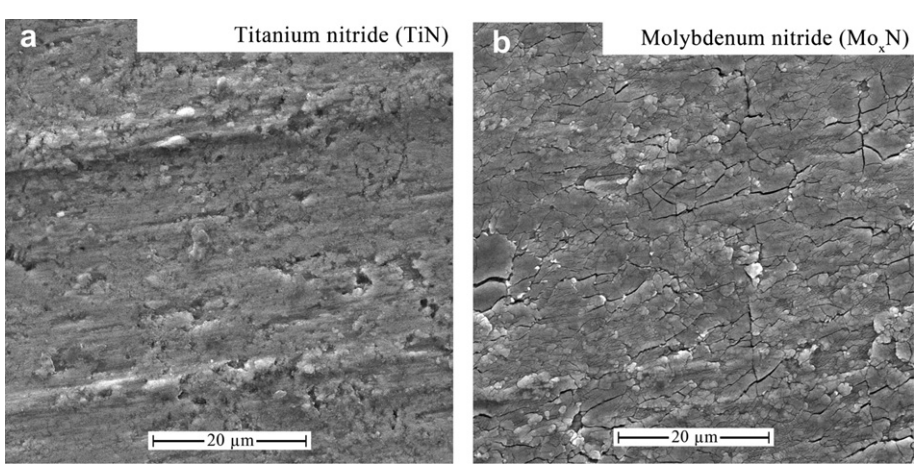

Fig. 2. SEM micrographs for (a) titanium nitride (TiN) electrodes and (b) molybdenum nitride (Mo_xN) on titanium substrate electrodes.