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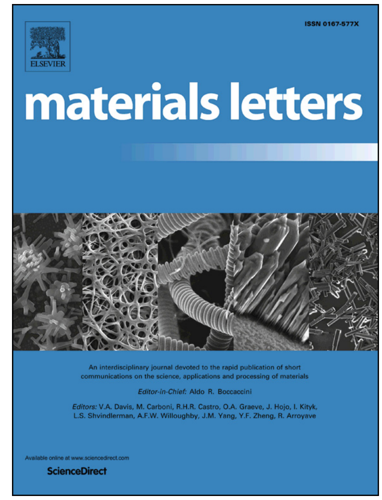

Egg shell membrane template stabilises formation of β-$NiMoO_4$ nanowires and enhances hybrid supercapacitor behaviour

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Egg shell membrane template stabilises formation of β-$NiMoO_4$ nanowires and enhances hybrid supercapacitor behaviour

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Abstract
Adding an eggshell membrane (ESM) template to the solution combustion synthesis of $NiMoO_4$ resulted in the formation of β-$NiMoO_4$ under mild conditions. It is postulated that the unique nature of the ESM template results in interactions that stabilise this difficult to synthesise form of $NiMoO_4$.The ESM template led to β-$NiMoO_4$ particles that were nano-wire like in shape and arranged in an open weave structure that significantly enhanced the mesoporosity and conductance of the material. The specific capacitance was measured as 259 F g^{-1} in a two electrode system with an energy density of 252.2 W h kg^{-1}. The results indicate that the use of a fibrous like natural polymeric materials as templates stabilises materials in preferred crystal forms and shapes leading to much improved electrochemical performance.

Keywords
Superconductors, Energy storage and conversion, Nickel molybdate, template, nanowire, eggshell membrane

1 Introduction

Large-scale uptake of clean and sustainable energy generation has led to much effort being devoted to the development of novel energy storage solutions to cater for the intermittent nature of the energy output from these renewable sources [1-6]. Supercapacitors are considered a promising technology in this area as they provide higher power and energy density than traditional batteries coupled with fast recharge ability, high energy storage capability, good rate performance, and long cycling stability [7]. Traditionally, supercapacitors have been available in two forms based on their charge storage mechanism. Electrical double-layer capacitors (EDLC) store energy at the electrode/electrolyte interface, while pseudocapacitors utilise electron transfer faradaic reactions in a suitable electrolyte. Hybrids of these traditional forms are now being actively investigated where both storage mechanisms can be accessed, resulting in devices with much higher capacitance and a broader range of applications [8,9].

An essential part of the development of hybrid supercapacitors is the investigation of novel active materials for electrode manufacture [10-12]. Mixed metal oxides are a promising area due to the availability of multiple oxidation states and relative earth abundant starting materials [13-16]. Mixed metal molybdates, especially those incorporating Ni, are particularly interesting materials, exhibiting high specific capacitance and energy density [17-20]. This improved performance is attributed to the fact that $NiMoO_4$ is more chemically active than other molybdates (Mg, Co, etc.) and exhibit a greater density of oxidation states near the top of the valence band [21,22].

There are two main ways to increase the performance of a hybrid supercapacitor electrode: increase the surface area and manipulate the material to improve conductance. The former can be achieved by synthesising nano-sized particles with interesting shapes or a porous nature that allow maximum access to the surface of the material or by simply increasing porosity without resorting to the nanoscale [23-25]. Improvement in conductance can be achieved by depositing a mixed metal oxide onto a suitably conductive surface, e.g. a conductive metal or graphene, and/or by ensuring a particular particle shape/crystal form is produced [26,27]. Some researchers have shown that using both approaches can improve electrochemical performance dramatically, e.g. growing $NiMoO_4$ on Ni foam [28] or graphene [20, 29-32]. Little work has been done on the use of polymeric templating agents. Use of such templates may have the benefit of producing a more flexible material that is better able to withstand the expansion and contraction of the electrode that occurs during the charge/discharge cycle and is so destructive to the long-term performance of energy storage devices.

Egg shell membrane (ESM) consists of interwoven coalescing fibres ranging in diameter from 0.5-1μm with pore sizes of 1-3μm [33] and has been used as a template to improve the porosity of numerous materials [34-37]. The material is cheap to source and produce as well as being environmentally benign [33]. Due to the presence of chelating functional groups in the proteinaceous fibres, it is possible that the ESM can stabilise particular crystal