Mechanistic insights into high lithium storage performance of mesoporous chromium nitride anchored on nitrogen-doped carbon nanotubes

Memona Idrees [a], Syed Mustansar Abbas [b,*], Ata-Ur-Rehman [c,d], Nisar Ahmad [e], Muhammad Waheed Mushtaq [f], Rizwan Ali Naqvi [g], Kyung-Wan Nam [b], Bakhtiar Muhammad [a], Zafar Iqbal [h]

[a] Department of Chemistry, Hazara University, Mansehra, Pakistan
[b] Department of Energy and Materials Engineering, Dongguk University, 30, Pildong-ro 1-gil, Jung-gu, Seoul 04620, Republic of Korea
[c] Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan
[d] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[e] Nanoscience and Technology Department, National Centre for Physics, Islamabad, Pakistan
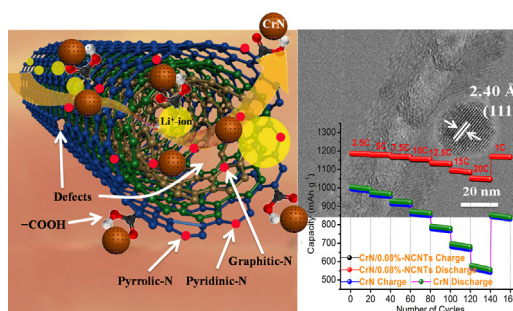[f] Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan
[g] Division of Electronics and Electrical Engineering, Dongguk University, 30, Pildong-ro 1-gil, Jung-gu, Seoul 04620, Republic of Korea
[h] Department of Physics, Faculty of Engineering & Applied Sciences, Riphah International University, I-14 Campus, Islamabad, Pakistan

HIGHLIGHTS

- Unique nanocomposite structure consists of mesoporous CrN with NCNTs homogenously distributed on surface.
- The CrN/0.08%-NCNT electrode retains a high capacity of 1042.9 mAh g^{-1} at 20 °C.
- The network structure with conductive electron paths enables high rate capability.
- The reversible conversion reaction mechanism of CrN into Cr metal and Li$_3$N is revealed.
- Pyridinic nitrogen has a high influence on the Li storage properties for NCNTs.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Chromium nitride (CrN) synthesized by heating at 550 °C under a continuous stream of ammonia has been investigated as anode material for lithium electrochemistry. Due to its low lithium insertion potential, Cr is an attractive material for lithium–ion battery application, but the usual volume variation effect obstructs its practical use. In this study, different concentrations of carbon nanotubes doped with nitrogen (NCNTs) are combined with CrN to attain high electrochemical performance. The synthesized CrN/0.08%–NCNTs nanocomposite demonstrates network structure with 30–40 nm CrN nanoparticles anchored to specific sites on 40–60 nm diameter NCNTs. Upon electrochemical testing, CrN/0.08%–NCNTs nanocomposite displays a discharge capacity of 1172 mAh g^{-1} after 200 cycles with high coulombic efficiency (∼100%) and rate capability. The electrode can deliver a reversible capacity of 1042.9 mAh g^{-1} at 20 C. The n-type concentration, along with the conductive CNTs framework, mesoporous channels, appropriate surface area and buffering capability of CNTs, are together responsible

* Corresponding author.
E-mail address: qau_abbas@yahoo.com (S.M. Abbas).

for the excellent electrochemical performance. The electrochemical reaction mechanism of CrN with lithium is explored by investigating the structural changes using *ex situ* X-ray photoelectron spectroscopy, X-ray diffraction, selected area electron diffraction, and high-resolution transmission electron microscopy. The reversible conversion reaction of CrN into Cr metal and Li$_3$N is revealed.

1. Introduction

Considerable research effort towards finding new electrochemically active materials for lithium–ion battery (LIB) electrodes has been conducted over the last two decades. Much of this research has focused on the transition metal-based compounds, due to their potential advantages [1–3]. Recently, transition metal nitrides have been considered as active materials for electrodes of LIBs, due to their low and flat potential that is comparable to lithium, with reversible kinetics, and large theoretical capacity, involving three moles of Li per mole of formula unit [4,5]. In the recent past, nitride materials have attracted considerable attention from researchers for electrochemical applications [6–9].

Chromium nitride (CrN) is amongst the few materials with excellent properties, like hardness, chemical stability, conductivity, and reflectance, for diverse applications that include corrosion resistance coatings [10], magnetics, electronics, solar selective absorbers, fuel cells, and high-temperature ceramics [4,11–13]. Although CrN has previously been synthesized using various multistep methods, like metal-plasma ion implantation, ion-beam deposition, pulsed laser deposition, hybrid PVD process, plasma nitridation of metal oxides, solid state metathesis, and pyrolysis of coordination compounds, these methods have involved many complications [14,15]. However, the direct nitridation of Cr$_2$O$_3$ nanoparticles in the flow of nitrogen containing source is by far the most adapted and convenient route for the synthesis of CrN nanoparticles, as it avoids toxic gases, complex organometallic reactions, high economics, and severe experimental conditions [11]. CrN forms *fcc* crystal structure with N-atoms occupying octahedral symmetry, providing an excess of free electrons for electronic conductivity [16]. Generally, the metal-based electrodes suffer from poor capacity retention, due to aggregation, loss of contacts on pulverization, and low Li$^+$–ion diffusion [17].

The use of carbonaceous supports, especially carbon nanotubes (CNTs), is an approach to solve these drawbacks, and further adds to the electrode performance by facilitating both Li$^+$–ion transport and electrons flow, along with acting as a shock absorber to reduce the pulverization and aggregation of metal nanoparticles [18,19]. Nitrogen is highly favorable for doping carbon-based anodes due to its comparable atomic size and five valence electrons for bonding with carbon [20,21]. The doping of N-atoms in the backbone of CNTs (NCNTs) is thought to supplement the conductivity of CNTs by adding more electrons and extrinsic defects. NCNTs are reported to have improved charge transport, electrolyte accessibility, and high conductivity, due to substitutional heteroatoms in graphene layers and regular porous structure [22,23]. N-atoms in the CNTs enhance the reactivity towards metal nanoparticles, making them attach more tightly to the CNTs surface [24].

Unlike transition metal oxides, there is very limited research on the metal nitrides for electrochemical energy storage. Mostly, two-fold transition metal nitrides M$_x$N$_y$ (M = Sn, Zn, Cu, Ge, Fe, Co, Cr, Ni, V, Mn, Ti) [25,26], some lithiated transition metal nitrides Li$_x$-MN$_y$ (M = Mn, Mo, Fe, Co) and N-doped metal oxides [27–29] are reported for electrochemical energy storage applications [8,9,30]. Some of these metal nitrides react through a two-step conversion process that involves reduction of metal and secondary alloying process [31], while others are found to totally or partially react

by yielding Li$_3$N and metal, without forming any alloy [32]. It is worth considering that such a nanocomposite made from CrN on NCNTs has not previously been achieved. In this paper, we report experimental findings on the synthesis of CrN and its nanocomposite with NCNTs, and its electrochemical properties as an anode for LIBs, along with the mechanism of its high electrochemical activity.

2. Experimental

2.1. Sample preparation

All the chemicals used in this work were purchased from Sigma–Aldrich and were of the analytical grade, so no further purification was needed. CNTs were synthesized by using a chemical vapor deposition method (CVD), using porous nickel foam loaded with iron-based catalyst. Pure CNTs were formed with nickel acting as an active catalyst, as well as a substrate, with the combination of iron nanoparticles. A substrate loaded with the suitable amount of Fe(OH)$_3$ was carefully placed in a quartz tube, which was then fixed in a tube furnace. Firstly, by passing a combination of H$_2$ and Ar at 40 sccm at 400 °C, the catalyst was activated, after which the temperature was raised to 600 °C, and acetylene gas (C$_2$H$_2$) at a flow rate of 60 sccm was passed over the activated catalyst. The synthesized raw CNTs were collected after 2 h.

In order to remove the trapped metal catalyst, raw CNTs were refluxed in 6 M HCl for 3 h, followed by neutralization, and drying at room temperature. Functionalization of purified CNTs (fCNTs) was carried out by treatment with a 1:1 mixture of HNO$_3$ (5 M) and H$_2$O$_2$ (30%) under constant ultrasonication for 6 h, followed by repeated centrifugation at 12,000 rpm, washing to attain neutral pH, and finally, drying at 80 °C [33].

The synthesis of CrN/x%–NCNTs (x = 0.0, 0.02, 0.04, 0.08, 0.2) nanocomposites is carried out by the nitriding of Cr$_2$O$_3$/x%–fCNTs nanocomposites. Cr$_2$O$_3$/x%–fCNTs is earlier formed by suspending stoichiometric amounts of CrCl$_3$ and fCNTs in 0.1 M polyvinylpyrrolidone (PVP) solution under ultrasonication for 30 min, followed by titration from 0.2 M NaOH solution under continuous stirring, until pH of 12 is attained. The mixture is left for stirring overnight, after which precipitates are filtered and washed with an excess of distilled water until the filtrate comes out neutral. The precipitates are dried at 80 °C and finally annealed at 450 °C for 4 h in argon, to obtain Cr$_2$O$_3$/x%–f–CNTs. The CrN/x%–NCNTs is formed by calcination of Cr$_2$O$_3$/x%–fCNTs at 550 °C under a constant stream of ammonia gas for 12 h. CrN/0.08%–NCNTs nanocomposite demonstrated the best electrochemical performance.

2.2. Sample characterization

The composition and phase purity of the samples before and after electrochemical reactions was determined through Bruker-D8 powder X-ray diffractometer (XRD) equipped with Cu-Kα radiation of wavelength 1.5418 Å. Fourier-transform infrared (FTIR) spectra of samples were recorded by FTIR-Thermo Nicolet-6700 analyzer to determine the presence of various functional groups. The specific surface area and pore size distribution of samples were calculated by means of the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, using the Coulter-SA-3100