Synergistic Role of Electrolyte and Binder for Enhanced Electrochemical Storage for Sodium-Ion Battery

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ABSTRACT: Sodium-ion batteries are promising futuristic large-scale energy-storage devices because of the abundance and low cost of sodium. However, the development and commercialization of the sodium-ion battery solely depends on the use of high-capacity electrode materials. Among the various metal oxides, SnO2 has a high theoretical specific capacity for sodium-ion battery. However, the enormous volume expansion and low electrical conductivity of SnO2 hinder its capability to reach the predicted theoretical value. Although different nanostructured designs of electrode materials like SnO2 nanocomposites have been studied, the effects of other cell components like electrolyte and binder on the specific capacity and cyclic stability are yet to be understood. In the present study, we have investigated the synergistic effect of electrolyte and binder on the performance enhancement of SnO2 supported on the intertwined network structure of reduced graphene oxide partially open multiwalled carbon nanotube hybrid as anode in sodium-ion battery. Our result shows that sodium carboxyl methyl cellulose and ethylene carbonate/diethyl carbonate as the electrolyte solvent offers a high specific capacity of 688 mAh g\(^{-1}\) and a satisfactory cyclic stability for 500 cycles. This is about 56% enhancement in specific capacity compared to the use of poly(vinylidene fluoride) binder and propylene carbonate as the electrolyte solvent. The present study provides a better understanding of the synergistic role of electrolyte and binder for the development of metal-oxide-based electrode materials for the advancement of the commercialization of sodium-ion battery.

1. INTRODUCTION

Electrochemical energy-storage devices characterized by low cost and high efficiency have become attractive in the modern society especially in the field of portable electronic devices and sustainable grid power supply. The high energy density, long cycle life, and high efficiency are the reasons for the success of lithium-ion batteries (LIBs) in different sectors of energy-storage applications. But the limited global distribution of lithium makes future investment on lithium-ion battery for large-scale energy-storage systems high.1–3 Considering the cost and limited availability of lithium (20 ppm in Earth’s crust), more attention has been shifted to the identification and development of an alternative economically sustainable secondary battery. In this aspect, sodium is gaining much prominence for large-scale application in the current scenario due to its high abundance (2.83% in Earth’s crust and 30.6% in ocean) and low cost. In contrast to lithium, sodium ions have larger ionic radii (102 pm for Na\(^+\) and 76 pm for Li\(^+\)) and higher redox potential, thus reducing the energy density.4 The commercially used graphite anode in lithium-ion battery cannot reversibly store sodium ions because the formation of the binary graphite intercalation compound is energetically unfavorable.5–6 Hard carbon has a disoriented structure and shows a reversible capacity of 300 mAh g\(^{-1}\) when used as an anode in sodium-ion battery.7 But sodium-intercalated hard carbon reacts with nonaqueous electrolytes reducing the stability of the electrode, which is a major concern.7 These challenging factors have increased the need to develop a suitable host material, which can reversibly store sodium ions with good cyclic stability.

Electrode materials based on the mechanism of alloying like Sn and Sb show 2–3 times higher specific capacity compared to intercalation-based materials.8 Among the alloying-based materials, SnO2 has drawn much attention because of its high theoretical specific capacity of 667 mAh g\(^{-1}\), chemical stability, and environment-friendly nature.9,10 But SnO2 has slow reaction kinetics with sodium, causing irreversible conversion reaction, and thus the reversible capacity arises from alloying reaction alone. The alloying reaction of sodium with Sn causes huge volume expansion (420%), leading to pulverization and agglomeration of nanoparticles, resulting in capacity fading.11–14 To alleviate these problems, several strategies have
been adopted. Reducing the size of SnO$_2$ to nanosize can provide a short diffusion path for the movement of electrons and ions, large electrode/electrolyte contact area, and more active sites for sodium storage. Another technique has been employed to enhance the reaction kinetics where a conductive carbon support is used along with SnO$_2$, which acts as a buffer layer for alleviating volume expansion. But the use of amorphous carbon as carbon support gives poor rate capability because of its low electronic conductivity. Carbon supports like graphene and multiwalled carbon nanotubes (MWNTs) have excellent electronic conductivity, large specific surface area, and high mechanical strength. It has been reported that ultrafine SnO$_2$ nanoparticles on reduced graphene oxide (rGO) delivers a reversible specific capacity of 324 mAh g$^{-1}$ at 50 mA g$^{-1}$. After 100 cycles at 100 mA g$^{-1}$, the cell delivers a specific capacity of 369 mAh g$^{-1}$. Wang et al. demonstrated that SnO$_2$ quantum dots with graphene aerogel delivers a specific capacity of 319 mAh g$^{-1}$ at 50 mA g$^{-1}$ after 50 cycles. They also reported that SnO$_2$ on MWNTs delivers a specific capacity of 500 mAh g$^{-1}$, which is 71% of the theoretical specific capacity. Amorphous SnO$_2$ coated on MWNTs provides an enhanced specific capacity of 630 mAh g$^{-1}$ at 100 mA g$^{-1}$. The amorphous nature of SnO$_2$ increases the $d$ spacing, which facilitates faster diffusion of sodium ions, thereby enhancing the reversible conversion reaction of sodium ions with SnO$_2$. The combination of reduced graphene oxide and MWNTs accommodates volume expansion as well as provides faster reaction kinetics during the alloying reaction. Although reduced graphene oxide and MWNTs have superior electronic conductivity and faster reaction kinetics, still some critical issues are not solved. The electrical contact between SnO$_2$ and carbon support gets broken due to the repeated expansion and shrinkage of SnO$_2$ during cycling. This leads to capacity decay and poor cyclic stability. Although the active material determines the energy-storage, the electrolyte and electrolyte also have a major impact on the cyclic stability and rate capability. The effect of electrolyte and binder on the performance of metal-oxide/carbon composites in a sodium-ion battery is less discussed and developed compared to electrode materials. The commercialization of metal oxides with an effective performance and stability can only be achieved by selecting the optimum parameters like electrolyte and binder along with suitable electrode material. Propylene carbonate (PC) is the most common solvent used in LIB and sodium-ion battery due to its higher dielectric constant and thermal stability. But the use of propylene carbonate alone causes the formation of an unstable solid electrolyte interphase (SEI) layer, leading to electrolyte decomposition and capacity fading during cycling. Ethylene carbonate (EC) provides a stable electrolyte interface layer and thus helps in enhancing the cyclic stability of the electrode. The use of binary solvents improves the ionic conductivity by enhancing the dissociation of the salt and lowering the viscosity of the electrolyte. The effect of salt and solvent in the electrolyte on the performance of hard carbon electrode has been discussed for sodium- and lithium-ion batteries. It was found that the electrolyte solvent remarkably affects the electrochemical performance of hard carbon anode rather than the electrolyte salts. Along with the electrolyte, the binder also plays a crucial role for improving the performance of the battery. Poly(vinylidene fluoride) (PVDF) is the most commonly used binder because of its good electrochemical stability and binding capability. The effect of using water-soluble sodium polyacrylic acid as binder reduces the internal resistance compared to conventional PVDF binder, thereby enhancing the Coulombic efficiency and cyclic stability of nitrogen-doped carbon nanotubes.

In this work, to provide a good adhesion as well as electrical conductivity to SnO$_2$ nanoparticles, an attempt is made to use hybrid carbon nanostructures of partially open MWNTs (POCNT) and rGO as the conductive support. This unique morphology of POCNT with hydroxyl and carboxyl functional groups attached over the layers helps to form a suitable intertwined network structure with reduced graphene oxide. Moreover, this rGO intertwined POCNT network structure (rGPNT) plays the dual role of accommodating the volume expansion of SnO$_2$ and as an active material for the sodium-ion storage. This study also focuses on the experimental insight into the effect of binder and electrolyte solvent on the rate capability and cyclic stability. It is found that PVDF binder and PC as the electrolyte solvent are not suitable for the formation of a stable SEI layer and subsequent degradation on the performance of the electrode occurs. The excellent electrochemical performance of SnO$_2$rGPNT is obtained with Na-carboxymethyl cellulose (CMC) as binder and EC/diethyl carbonate (DEC) as the electrolyte solvent with a specific capacity of 688 mAh g$^{-1}$ at a current density of 50 mA g$^{-1}$, which is about 56% enhancement in capacity with respect to PVDF binder and PC electrolyte.

2. RESULTS AND DISCUSSION

The crystalline structure and the phase purity of the sample was determined by X-ray diffraction (XRD). The XRD patterns of rGO, POCNT, and SnO$_2$rGPNT are represented in Figure 1. rGO displays a broad peak at 24.5° indexed to (002) corresponding to exfoliated layers of reduced graphene oxide. In the XRD pattern of POCNT, a low-intensity peak is observed at 9.3° corresponding to an increase in the interlayer spacing of the few outer layers of MWNTs to 0.7 nm. The increase in $d$ spacing is due to the introduction of oxygen functional groups in the outer few layers of MWNTs. An intense peak at 26° is also observed corresponding to the C(002) plane with a $d$ spacing of 0.34 nm, which is due to the intact inner core of the MWNTs that remain unaffected during the process. The intense diffraction peaks in SnO$_2$rGPNT located at 26.1, 33.8, 37.7, 51.7, 65.1, and 78.2° can be indexed to the (110), (101), (200), (211), (301), and (321) planes, respectively, and are assigned to the tetragonal phase of SnO$_2$ (JCPDS card No. 00-001-0657). The lattice parameters are calculated to be $a = b = 4.738$ Å, $c = 3.187$ Å.

Thermogravimetric analysis was carried out to determine the SnO$_2$ loading in SnO$_2$rGPNT at a heating rate of 20 °C.
Figure 2. (a) Thermogravimetric analysis curves of SnO$_2$@rGPNT; (b) Raman spectra of rGO, POCNT, and SnO$_2$@rGPNT; (c) N$_2$ adsorption–desorption isotherm; and (d) pore size distribution of SnO$_2$@rGPNT.

Figure 3. XPS images of SnO$_2$@rGPNT: (a) survey spectrum, (b) C 1s, (c) O 1s, and (d) Sn 3d.
min$^{-1}$ in an air atmosphere, as shown in Figure 2a. A mass loss at 100 °C is due to the removal of water molecules present in the sample. A further mass loss of about 52% occurs at 500 °C due to the decomposition of POCNT and rGO. The mass loading of SnO$_2$ in SnO$_2$@rGPNT is calculated to be around 48%. The molecular vibrational characteristics of the sample were determined by Raman spectral analysis. The Raman spectra of all of the samples shown in Figure 2b indicate two major bands: D band around 1330 cm$^{-1}$ and G band around 1590 cm$^{-1}$. The G band corresponds to the characteristic peak of all graphitic carbon material arising due to $E_{2g}$ symmetry phonon mode, where the two atoms in the graphene unit cell are vibrating tangentially one against the other. The D band corresponds to the defects present in the edges and basal plane of MWNTs. The upshift of G band in POCNTs (Figure S1) is due to the electron transfer from the $\pi$ electron states of MWNTs to oxygen functional groups during the oxidation process and the strain developed due to the intercalation of functional groups into MWNTs, which results in the shortening of the C–C bond. The $I_D/I_G$ ratio defines the defect concentration in the material. The $I_D/I_G$ value for rGO, POCNTs, and SnO$_2$@rGPNT are observed to be 1.1, 1.13, and 0.93, respectively. The defect concentration in rGO and POCNTs is more due to the oxidation of graphitic structures by the functional groups, which creates the structural defects. Also, in the case of rGO, the sudden removal of the functional groups leaves defects in the structure. The defect concentration in SnO$_2$@rGPNT arises from SnO$_2$ nanoparticles, which get attached over the carbon network causing disorder in the structure and inducing defects. The downshift in peak for SnO$_2$@rGPNT is due to the transfer of electrons from rGPNT to SnO$_2$. This shift also implies that SnO$_2$@rGPNT composite is formed rather than an individual entity.

The nitrogen adsorption–desorption isotherm was employed to study the specific surface area and porosity of SnO$_2$@rGPNT. The porosity and surface area were measured using the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) method, respectively. Figure 2c displays a type IV isotherm, indicating mesoporous structure. The specific surface area calculated by the BET method is 209.48 m$^2$ g$^{-1}$, and the total pore volume is measured to be approximately 0.18575 cm$^3$ g$^{-1}$. The distribution of pore size calculated from the BJH plot has a maximum centered at 2.7 nm. The adsorption–desorption hysteresis indicates the presence of mesoporous structure. The presence of mesoporous structure facilitates relatively faster diffusion of sodium ions into the host structure with low ion-transport resistance.

To further investigate the chemical composition and oxidation state of SnO$_2$@rGPNT, X-ray photoelectron spectroscopy (XPS) analysis was carried out. The survey spectrum represented in Figure 3a shows the presence of elements like Sn, O, and C indicating the purity of the sample. The high-resolution (HR) spectrum shown in Figure 3b indicates the presence of C 1s and can be deconvoluted into four peaks located at 285.18, 286.23, 287.19, and 289.82 eV corresponding to the formation of C–C, C–O, C(O)O. The high-resolution spectrum of O 1s shown in Figure 3c is deconvoluted into four peaks located at 531.8, 532.9, 533.7, and 534.9 eV. The peak at 531.8 eV belongs to SnO$_2$, indicating the bond between Sn and O; the other peak positioned at 532.9 eV is assigned to C–O aromatic groups; the peak positioned at 533.7 eV is assigned to C–O–C epoxy groups, and the other peak at 534.9 eV corresponds to C–OH groups due to the presence of chemisorbed oxygen species. Two peaks with binding energies of 487.6 and 496.1 eV correspond to Sn 3d$^{5/2}$ and Sn 3d$^{3/2}$ as shown in Figure 3d.

The specific morphology of SnO$_2$@rGPNT was characterized by high-resolution transmission electron microscopy (TEM). The POCNTs intertwined with rGO and SnO$_2$ nanoparticles are distributed uniformly over the carbon support. SnO$_2$ forms a spherical morphology with a size...
range of less than 5 nm. It is well known that the size of the nanoparticles affects the electrochemical performance with the smaller particles offering better performance. The smaller size of the SnO₂ nanoparticles provides relatively less volume expansion compared to bulk, and the free space between the SnO₂ nanoparticles provides enough space for buffering the...
volume changes during sodiation and desodiation processes. The selected area electron diffraction (SAED) pattern (Figure 4d) is well indexed to the (110), (101), and (211) planes in the XRD pattern.

The electrochemical characteristics of SnO$_2$@rGPNT were initially evaluated by cyclic voltammetry (CV). Figure 5 shows initial four CV curves of SnO$_2$@rGPNT with CMC binder and EC/DEC as the electrolyte solvent in the potential range of 0.01–2.8 V at a scan rate of 0.1 mV s$^{-1}$. The first cathodic broad peak around 0.5–0.01 V is due to the decomposition of electrolyte resulting in the formation of SEI layer on the surface of electroactive material and the irreversible conversion reaction of SnO$_2$ to Sn. This peak covering a broad range has disappeared in the further cycles due to the irreversible and stable nature of the SEI layer formation. In further cycles, the cathodic peak positioned at 1.04 V is ascribed to the irreversible conversion of SnO$_2$ to Sn in reaction (1). The cathodic peak at 0.48 V is due to the alloying reaction of Na with Sn to form Na$_x$Sn as in reaction (2). The oxidation peak in the anodic region around 1.2–1.5 V is due to the reversible dealloying reaction of Na$_x$Sn. The redox peak around 0.1 V is ascribed to the insertion of sodium ions into the carbon structure. To further investigate the electrochemical characteristics of the electrode in different electrolytes and using different binders, CV curves are also recorded for CMC PC, PVDF EC/DEC, and PVDF PC, as shown in Figure S2, which also show similar behavior.

\[
\text{SnO}_2 + \text{Na}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Na}_2\text{O} \quad (1)
\]

\[
x\text{Na}^- + \text{Sn} + xe^- \rightarrow \text{Na}_x\text{Sn} \quad (0 \leq x \leq 3.75) \quad (2)
\]

Figure 5b shows the first cycle CV curves of SnO$_2$@rGPNT in different electrolytes and binders. The irreversible cathodic current for CMC is lower than that for PVDF, which indicates that CMC favors the formation of a stable passivation layer on the electrode. The electrode with PVDF binder and PC as electrolyte solvent shows more cathodic current due to the rapid decomposition of PC leading to thicker SEI layer formation.

Figure 6a–d represents the charge–discharge profiles of SnO$_2$@rGPNT with different electrolyte solvents and binders at different current densities in the potential range of 0.01–2.8 V. The charge–discharge profile shows a sloping and plateau region at low current density. But the plateau region is not obvious in the further cycles. Due to the irreversible binding of sodium with oxygen, distinct plateau is not observed in the further cycles. This is the characteristic potential profile feature of crystalline tin as reported in previous reports.$^{34,35}$ After repeated sodiation and desodiation, the amorphous nature of tin increases, which may not lead to the obvious plateau region in the charge–discharge profile.

The first cycle Coulombic efficiencies (FCCEs) of SnO$_2$@rGPNT electrodes with CMC EC/DEC, CMC PC, PVDF EC/DEC, and PVDF PC are calculated to be 49.61, 43.97, 27.82, and 25.76%, respectively. The low Coulombic efficiency in the first cycle is due to the irreversible loss of Na$^+$ ions in the process of SEI layer formation and the conversion of SnO$_2$ to Sn. This is consistent with the CV profile shown in Figure 5. The high FCCE of SnO$_2$@rGPNT clearly reveals that the effective surface passivation occurs with CMC binder and EC/DEC as the electrolyte solvent. The improved FCCE with CMC binder compared to PVDF is due to the presence of more carboxyl functional groups attached to CMC, enabling the formation of effective surface passivation irrespective of electrolyte solvent. CMC is a linear polymeric derivative of cellulose with carboxymethyl substitution. CMC provides better adhesion and dispersion of the electrode slurry. It is already proved that the –OH group present in the CMC does not contribute to the irreversible capacity. Therefore, the –OH group present in the CMC binder does not affect the FCCE. Therefore, the good adhesion provided by CMC offers better FCCE compared to PVDF$^{56}$ and hence the CMC binder plays a significant role in improving the FCCE.

As seen from the charge–discharge curves, the discharge capacities obtained at 50 mA g$^{-1}$ are 688, 478, 580, and 450 mAh g$^{-1}$, respectively, for CMC EC/DEC, CMC PC, PVDF EC/DEC, and PVDF PC. When cycled at 500 mA g$^{-1}$, the discharge capacities decreased to 278, 100, 92.41, and 1 mAh g$^{-1}$, respectively, corresponding to capacity retentions of 40.4, 20.92, 15.93, and 0.2% compared to the specific capacity of 50 mAh g$^{-1}$. These results confirmed that the PVDF binder cannot endure huge volume expansion of the electrode at higher current density, thereby resulting in the pulverization due to which a new electrode surface is exposed to the electrolyte and thus SEI layer is formed continuously. This process results in low capacity and poor cyclic stability.

Figure 6e displays the rate capabilities of SnO$_2$@rGPNT. Upon raising the current density stepwise from 50 to 100, 200, 500 mA g$^{-1}$, and 1 A g$^{-1}$, SnO$_2$@rGPNT with CMC EC/DEC remarkably shows excellent reversible stable capacities of 688, 451, 363, 278, and 113 mAh g$^{-1}$, respectively, which are higher than those for CMC PC, PVDF EC/DEC, and PVDF PC. This further elucidates that better electrochemical performance can be obtained with the proper selection of binder and electrolyte. Since SnO$_2$@rGPNT with CMC EC/DEC shows better rate capability, the understanding of the contribution of rGPNT in
the composite structure to the specific capacity is inevitable. In this aspect, rGPNT without SnO\textsubscript{2} is evaluated by using charge–discharge studies. Figure S3 indicates the rate capability of rGPNT with CMC as binder and EC/DEC as the electrolyte solvent. The rate capability curve shows specific capacities of 214, 156, 122, 102, and 72 mAh g\textsuperscript{−1} at 50, 100, 200, 500 mA g\textsuperscript{−1}, and 1 A g\textsuperscript{−1}, respectively. The reversible specific capacity contribution from rGPNT is about 30%, and the major contribution of reversible specific capacity is obtained from SnO\textsubscript{2} in the SnO\textsubscript{2}@rGPNT composite. In rGPNT, the sodium ions are stored by the process of adsorption into the defect sites as well as intercalation into the carbon structure. The intertwined structure of reduced graphene oxide and multiwalled carbon nanotubes acts as a good conducting support for the uniform dispersion of SnO\textsubscript{2} as well as an active material for sodium-ion storage.

Inspired by the excellent rate capability of SnO\textsubscript{2}@rGPNT, the long-term cyclic stability of SnO\textsubscript{2}@rGPNT in different electrolytes and binders is further studied at a current density of 200 mA g\textsuperscript{−1}. Figures 6f and 7 represent the cyclic stabilities of the electrode for 100 and 500 cycles, respectively. SnO\textsubscript{2}@rGPNT with CMC binder and EC/DEC electrolyte shows excellent cyclic stability with capacities of around 280 and 98 mAh g\textsuperscript{−1} after 100 and 500 cycles, respectively. When PVDF is used as the binder, the specific capacities obtained are around 117 and 31 mAh g\textsuperscript{−1} after 100 cycles for EC/DEC and PC, respectively. The presence of PVDF around the metal-oxide particles cannot endure huge volume changes resulting from the process of alloying and dealloying. Therefore, pulverization of the electrode leads to the continuous formation of SEI layer, resulting in poor cyclic stability.

To further understand the electrode reaction kinetics, cyclic voltammetry was carried out in the broad scan rate of 0.1–1 mV s\textsuperscript{−1} and for CMC EC/DEC, the CV curve is shown in Figure 8a, and for CMC PC, PVDF EC/DEC, and PVDF PC, the CV curves are shown in Figure S4. The maximum anodic peak current, as shown in Figure 8a, is plotted against the square root of the scan rate. Their linear relationship shown in Figure 8b indicates the diffusion-controlled reaction, where the Randles–Sevcik equation is applicable.

\[
I_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}Cv^{1/2}
\]  

where \(I_p\) is the peak current; \(n\) is the number of electrons transferred; \(A\) is the surface area of the electrode; \(D\) is the diffusion coefficient; \(C\) is the concentration of Na\textsuperscript{+} ions in the electrode material; and \(v\) is the scan rate. The linear relationship between peak current and square root of the scan rate indicates that the process is a diffusion-controlled process. The slope of the linear curve with CMC EC/DEC shows a higher value compared to CMC PC, PVDF EC/DEC, and PVDF PC, which indicates higher diffusion of Na\textsuperscript{+} ions in CMC EC/DEC. This higher diffusion of Na\textsuperscript{+} ions in CMC EC/DEC shows better performance, which is consistent with the rate capability and cyclic stability curves.
To obtain a better understanding of electrons and ion transfer across the electrode/electrolyte interface, electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10 mHz to 100 kHz at the voltage amplitude of 5 mV s\(^{-1}\). To analyze and compare the electrochemical impedance in CMC EC/DEC, CMC PC, PVDF EC/DEC, and PVDF PC, EIS was carried out on the electrodes after 30 cycles. Electrochemical impedance was fitted with the equivalent circuit, as shown in Figure 9a. The equivalent circuit model consists of resistance of the electrolyte and ohmic resistance (\(R_s\)), surface film resistance (\(R_2\)), relax capacitance (\(Q_1\)), charge-transfer resistance (\(R_3\)), double-layer capacitance (\(Q_2\)), and Na\(^+\)-ion bulk diffusion resistance (\(W_3\)).

The Nyquist plot is fitted using the EC lab software. The equivalent circuit consists of a semicircle in the high-frequency region and a vertical line in the low-frequency region. The charge-transfer resistance for SnO\(_2\)@rGPNT with PC electrolyte is much higher compared to that for EC/DEC. The continuous decomposition of PC leads to the formation of a thicker SEI layer, which provides much higher resistance for the diffusion of ions. This further confirms the reason behind the enhanced rate capability of SnO\(_2\)@rGPNT with EC/DEC electrolyte. The charge-transfer resistance of SnO\(_2\)@rGPNT with CMC EC/DEC is low compared to all other combinations of electrolyte and binder. The mechanical instability of PVDF leads to the rapid decomposition and has higher charge-transfer resistance, whereas CMC, which is a cross-linked polymer, has higher mechanical strength and can endure huge volume expansion that happens during the process of repeated alloying and dealloying.\(^{37}\)

Further EIS data in the low-frequency region were used to calculate the diffusion coefficient according to the following equation

\[
D_{\text{Na}} = \frac{R^2T^2}{2A^4n^4F^4C^2\sigma^2}
\]  

(4)

where \(R\) is the gas constant, \(T\) is the temperature, \(A\) is the area of the electrode, \(F\) is the Faraday constant, \(C\) is the concentration of the sodium ions in the electrolyte, and \(\sigma\) is the Warburg factor, which can be taken from the slope of the linear plot of the real impedance versus minus square root of the frequency. The Warburg factors obtained for PVDF PC, PVDF EC/DEC, CMC PC, and CMC EC/DEC are 67.31, 146.76, 140.35, and 23.38 respectively. According to eq 3, the low Warburg factor gives higher diffusion coefficient. SnO\(_2\)@rGPNT with CMC as binder and EC/DEC as electrolyte solvent shows lower Warburg coefficient, which signifies higher diffusion coefficient. This contributes to the enhanced performance in terms of sodium-ion storage.

To further understand the SEI layer formation in different electrolytes and binders, cross-sectional microscopy images were obtained for the fresh electrodes as well as for the cycled electrodes. For the electrodes before cycling, there is no formation of surface films. For the cycled electrode, there is a formation of surface films on the surface of the electrode, as shown in Figure 10b,c,e,f. The surfaces of PVDF PC and PVDF EC/DEC after cycling appear to be rough, which can be due to the decomposition of the electrolyte during the process of repeated charging and discharging. In the case of CMC EC/DEC, as shown in Figure 10f, the roughness of the SEI layer formed is less compared to PVDF PC, PVDF EC/DEC, and CMC PC. This allows to maintain the structural stability of the...
electrode even after cycling. This is due to the fact that the SEI layer formed is thin, which is highly essential to enhance the better transport of ions into the electrode by lowering the charge-transfer resistance. This is evident from the EIS measurement analysis (Table 1), where the charge-transfer resistance is very less and therefore enhancement in specific capacity is obtained.

Table 1. Calculated Electrolyte Resistance, SEI Film Resistance, and Charge-Transfer Resistance from Nyquist Plot for Cycled SnO2@rGPNT

| sample name     | Rs (Ω) | Rf (Ω) | Rct (Ω) |
|-----------------|--------|--------|---------|
| PVDF PC         | 7.72   | 32.43  | 366.7   |
| PVDF EC/DEC     | 3.441  | 5.832  | 219.4   |
| CMC PC          | 2.636  | 9.453  | 294.5   |
| CMC EC/DEC      | 6.382  | 3.244  | 126.2   |

The surface of the fresh electrode and cycled electrode is analyzed using the SEM images (Figure 11). The surface of the fresh electrode has no thin layer, and there are few pores observed, which helps in the diffusion of electrolyte ions into the electrode. After cycling of the electrodes, it can be observed that there is a formation of a layer on the surface of the electrode. In the case of PVDF PC, the morphological image shows that the surface of the electrode is covered by a very thick SEI layer because there are no pores observed on the electrode surface after cycling (Figure 11b). This results in an increase in the resistance to the movement of sodium ions into the electrode material and subsequently results in low specific capacity and poor cyclic stability. Also, at higher current density, due to the higher resistance offered by the SEI layer, the interaction of sodium ions with the electroactive material is limited, resulting in very poor rate capability. For CMC EC/DEC, the surface morphology does not show any changes even after cycling. The formation of thin SEI layer enables better diffusion of sodium ions and helps in achieving better rate capability and cyclic stability. The presence of different elements in the SEI layer has been analyzed by energy-dispersive X-ray spectroscopy (EDAX) mapping, as shown in Figure S2. The presence of different elements like Na, Sn, O, C, and Cl indicates the formation of SEI layer.

3. CONCLUSIONS

In summary, optimized loading of ultrafine SnO2 anchored on intertwined reduced graphene oxide partially open carbon nanotube hybrid, synthesized by a simple polyol reduction method, used as anode in Na-ion battery, provides sufficient specific capacity and rate capability. The effect of the electrolyte and binder on the specific capacity and cyclic stability emphasizes that PC electrolyte solvent and PVDF binder are not suitable for the formation of a stable SEI layer and retaining the cyclic stability, while the use of Na-CMC binder and EC/DEC as the electrolyte solvent has a positive impact on the first cycle Coulombic efficiency and cyclic stability. Besides, the use of a cross-linked polymer like Na-CMC provides good adhesion and prevents the collapse of the electrode during the enormous volume expansion of metal oxides. This work reveals that in addition to the investigation of the different structural modification of the anode electrode, further investigation on the electrolyte and binder can lead to a new direction for the commercialization of metal-oxide-based carbon composites as anode in sodium-ion battery.

Figure 11. SEM image of (a) SnO2@rGPNT PVDF before cycling, (b) cycled SnO2@rGPNT PVDF PC, (c) cycled SnO2@rGPNT PVDF EC/DEC, (d) SnO2@rGPNT CMC before cycling, (e) cycled SnO2@rGPNT CMC PC, and (f) cycled SnO2@rGPNT CMC EC/DEC.
4. EXPERIMENTAL SECTION

4.1. Method of Preparation of SnO$_2$@rGPNT. Graphite oxide was prepared by Hummers’ method. Graphite was oxidized by strong oxidizing agents like KMnO$_4$ and NaNO$_3$ in the presence of concn H$_2$SO$_4$ at ice temperature and stirred for 1 h. After that, 90 mL of warm deionized (DI) water was added to the above mixture and stirred for 1 h. To make the mixture more dilute, 292 mL of DI water was added. Then, 12 mL of hydrogen peroxide was added to remove the unreacted compounds in the mixture. The solution was filtered, washed several times with DI water until the pH was neutral, and dried at 60 °C overnight. rGO was prepared by hydrogen reduction of graphite oxide at 200 °C in an argon atmosphere.

Partially open multiwalled carbon nanotubes (POCNTs) were prepared by introducing functional groups on the outer few layers of multiwalled carbon nanotubes (MWCNTs) by Hummers’ method. MWCNTs were synthesized by the catalytic chemical vapor deposition technique. Misch metal and nickel-based AB$_2$ alloy were used as the catalysts for the growth of MWCNTs. The growth of MWCNTs was carried out at 700 °C in an argon atmosphere using acetylene gas as the carbon precursor. The obtained MWCNTs were further air-oxidized at 450 °C in an air atmosphere and acid-treated with HNO$_3$ to remove amorphous carbon and metal particles, respectively.

SnO$_2$@rGPNT was synthesized by dispersing a 1:1 weight ratio of rGO and POCNTs in a mixture of ethylene glycol and water. To this solution, 450 mg of SnCl$_2$$\cdot$2H$_2$O was added and stirred for 12 h for the uniform dispersion. Then, NaOH was added to maintain the pH of the solution at 12. The final solution was refluxed at 120 °C and then filtered, washed, and dried at 80 °C to obtain the final product. rGPNT without SnO$_2$ is obtained by the similar method without the addition of SnCl$_2$$\cdot$2H$_2$O.

4.2. Material Characterization. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). All measurements were taken in the range of 5–90° with the step size of 0.02°. Raman spectra were recorded using a WiTec α Raman spectrometer in the range of 500–3000 cm$^{-1}$. The laser source used was Nd:YAG (532 nm). Thermogravimetric analysis was carried out in SDT Q600 analyzer from TA Instruments in an air atmosphere from room temperature to 1000 °C at a heating rate of 20 °C min$^{-1}$ with a flow rate of 160 mL min$^{-1}$. The surface area and pore size analysis were done using Micromeritics ASAP 2020 instrument using the Brunauer—Emmett—Teller (BET) theory. To study the morphology of the samples, high-resolution transmission electron microscope (HRTEM) images were recorded in a Technai G20 instrument by drop-casting sample solution in ethanol on holey carbon coated 200 mesh copper grids. X-ray photoelectron spectroscopy (XPS) was carried out in a Specs X-ray photoelectron spectrometer with Mg Kα as the X-ray source and PHOIBOS 100MC analyzer.

4.3. Electrochemical Characterization. The slurry for the electrode was prepared by mixing 75% of SnO$_2$@rGPNT, 10% of acetylene black, and 15% of two different binders, namely, poly(vinylidene fluoride) (PVDF) and sodium carboxymethyl cellulose (CMC), in N-methyl-2-pyrrolidone and water, respectively. The working electrodes were prepared by coating the slurry on copper foil and then dried at 80 °C overnight in a vacuum oven. The dried electrodes were cut in the form of circular disks of 12 mm diameter. The typical active material loading was 0.9–1 mg cm$^{-2}$. 2032-Coins cells were assembled in an argon-filled glovebox, where the oxygen and moisture levels were maintained below 0.1 ppm. Sodium metal was used as the counter electrode and reference electrode with glass fiber membrane (Whatman GF/C) as the separator. The electrolyte used was 1 M NaClO$_4$ dissolved in two different solvents, propylene carbonate (PC) and ethylene carbonate/diethyl carbonate (EC/DEC 1:1 v/v). The cells were galvanostatically cycled at various current densities between 0.01 and 2.8 V on a Bio-Logic BCS 810 battery cycler. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on Bio-Logic SP 300. Electrochemical impedance spectroscopy (EIS) was conducted by applying an AC signal of amplitude 5 mV in the frequency range of 10 mHz to 100 kHz. The cyclic voltammetry was carried out in the potential range of 0.01–2.8 V at different scan rates of 0.1–1 mV s$^{-1}$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01407.

CV curves of SnO$_2$@rGPNT for CMC PC, PVDF EC/DEC, and PVDF PC for the first four cycles at the scan rate of 0.1 mV s$^{-1}$; rate capability curve of rGPNT with CMC EC/DEC; CV curves of SnO$_2$@rGPNT with PVDF PC, PVDF EC/DEC, and CMC PC at different scan rates; and EDAX mapping of fresh electrodes and cycled electrodes (PDF)

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Notes

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