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Chandni Devi

Central University of Rajasthan

Jnaneswari Gellanki

University of Delhi

Håkan Pettersson (✉ hakan.pettersson@hh.se)

Lund University

Sandeep Kumar

Central University of Rajasthan <https://orcid.org/0000-0002-5963-015X>

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High sodium ionic conductivity in PEO/PVP solid polymer electrolytes with InAs nanowire fillers

Chandni Devi¹, Jnaneswari Gellanki², Håkan Pettersson^{3, 4, *} and Sandeep Kumar^{1, *}

¹Department of Physics, Central University of Rajasthan, Ajmer-305817, India

²Department of Physics, University of Delhi, Delhi-110006, India

³Solid State Physics and NanoLund, Lund University, Box 118, SE-221 00 Lund, Sweden

⁴School of Information Technology, Halmstad University, Box 823, SE-301 18, Halmstad, Sweden

* corresponding authors: hakan.pettersson@hh.se, sandeep.kumar@curaj.ac.in

Abstract

Solid-state sodium ion batteries are frequently referred to as the most promising technology for next-generation energy storage applications. However, developing a suitable solid electrolyte with high ionic conductivity, excellent electrolyte-electrode interfaces, and a wide electrochemical stability window, remains a major challenge. Although solid-polymer electrolytes have attracted great interest due to their low cost, low density and very good processability, they generally have significantly lower ionic conductivity and poor mechanical strength. Nanoscale ceramic fillers are known to enhance the ionic conductivity of polymer electrolytes. Here, we report on the development of a low-cost composite solid polymer electrolyte comprised of poly(ethylene oxide), poly(vinylpyrrolidone) and sodium hexafluorophosphate, mixed with indium arsenide nanowires. We show that the addition of 1.0 percent by weight of indium arsenide nanowires increases the sodium ion conductivity in the polymer to $1.50 \times 10^{-4} \text{ Scm}^{-1}$ at 40° C. In order to explain this remarkable characteristic, we propose a new transport model in which sodium ions hop between close-spaced defect sites present on the surface of the nanowires, forming an effective complex conductive percolation network. Our work represents a significant advance in the development of novel solid polymer electrolytes with embedded engineered ultrafast 1D percolation networks for near-future generations of low-cost, high-performance batteries with excellent energy storage capabilities.

Key words: Sodium ion batteries, energy storage, solid polymer electrolyte, semiconductor nanowires, ionic conductivity

Sodium ion batteries (SIBs) have generated immense research interest as potential substitutes for lithium ion batteries (LIBs) because they offer comparable electrochemical performance at low cost. In addition, their major component, sodium, is readily available, and they do not employ problematic metals such as cobalt [1,2]. Next-generation batteries are expected to be characterized by low cost, high safety, and high energy density. One of the main challenges in high-performance battery technology is to develop highly conductive electrolytes suitable for efficient transport of ions between the electrodes. In recent years, solid polymer electrolytes (SPEs) have emerged as the most promising candidates to replace conventional flammable and potentially dangerous liquid electrolytes [3–6]. The safety and stability of SIBs can be significantly improved by using an SPE because they are inert, and leakage is not an issue. Stability is further improved by mitigating harmful dendrite growth on the sodium (Na) anode [3]. Other advantages of SPEs include lower interface resistances because of the short distance between the electrodes, higher mechanical strength and flexibility, shape versatility, light weight, and low cost [4]. An SPE plays a dual role, acting as both separator and electrolyte. It is composed of a soft polar polymer matrix as a carrier for directly dissolved metal salts. The most widely studied SPEs for SIBs use a poly(ethylene oxide) (PEO) matrix filled with Na salts, e.g. NaPF₆. For SIBs, PEO is the most widely studied polymer host because of its higher solubility for Na salts, its good structural and chemical stability, and the presence of flexible ethylene oxide segments and ether-bonded oxygen atoms [3,4]. Today's state-of-the-art SPEs (polymer-Na salt blends) exhibit an ion conductivity of around 10^{-6} Scm^{-1} , which is significantly lower than that of liquid electrolytes at room temperature and therefore restricts their use in commercial applications [2,7]. It is generally assumed that the highly crystalline structure of the polymers limits their ionic conductivity because it allows coupling between ionic motion and segmental motion and local relaxation of the polymer chains.

It follows that reducing the crystallinity of polymers is the best strategy to increase their conductivity [3]. Over the years, many attempts have been made to enhance conduction in SPEs using a variety of approaches, including polymer blending, and adding plasticizers or ceramic nanofillers [8–10]. The main advantage of polymer blends is that their physical properties are easily controlled by changing the composition and synthesis conditions. PEO blended with polyvinylpyrrolidone (PVP) exhibits a high ionic mobility due to the amorphous matrix support by the PVP. The carbonyl group (C=O) present in the side chains of PVP forms complexes with inorganic salts. It has been reported that (PEO-PVP)₈-NaPF₆ solid polymer composites have the highest ionic conductivity ($\sim 10^{-6}$ Scm⁻¹) and the best electrochemical properties [7,11]. These composites still do not have high enough conductivity for commercial applications, but this may be improved by adding fast ionic conductor fillers. Introducing nanomaterials into SPEs is very attractive because they typically improve the electrolyte performance significantly, in addition to being simple to prepare and mix with the polymer. In the last decade, extensive studies have focused on adding nanoscale fillers such as nanoparticles (NPs) and nanowires (NWs) of Al₂O₃, SiO₂, TiO₂, ZrO₂, and LiAlO₂ to polymer hosts to enhance the ionic conductivity of SPEs for LIBs [12–19]. In addition to improving ion transport properties, nanofillers also improve the mechanical and electrochemical stability of the batteries. To date, there have been only very few reports on the effect of nanofillers in Na⁺-based SPEs for SIBs [20]. It is generally accepted that the enhanced ion conductivity observed by adding nanoscale fillers is primarily due to a reduction of the polymer crystallinity. Moreover, extensive experimental investigations focused on the effects on the conductivity of adding ceramic nanoparticles have shown that a strong Lewis acid-base interaction between surface groups of the nanofillers and electrolyte ion species can increase the ion

conductivity [18,21-22]. However, as yet, no detailed theoretical model that includes all of the mechanisms involved in ion transport through SPEs has been developed.

It was recently reported that SPEs incorporating high-aspect-ratio NWs have a higher ionic conductivity than SPEs filled with nanoparticles [13]. This improvement was attributed to the much longer continuous ion conduction pathway when NWs are present, effectively forming a percolation network. To date, most studies have involved ceramic NW fillers. The main objective of the present work is to develop a fundamental understanding of the mechanisms governing Na^+ transport in SPEs filled with III-V semiconductor NWs. Polymer nanocomposites with semiconductor nanofillers have already been used in diverse applications including electromagnetic interface shielding, gas and biosensors, solar cells, and light-emitting diodes [23,24]. However, to the best of our knowledge, the electrochemical properties of SPEs filled with semiconductor NWs have not been explored previously. Recently, we reported on the synthesis of InAs NWs by a low-temperature solvothermal method [25]. Using this low-cost method, it is possible to grow high-quality NWs on a large scale and so provide a low-cost feedstock for use in SPEs. The addition of semiconductor NWs to SPEs is expected to bring new insights and develop our fundamental understanding of electrochemical interactions on a molecular scale, and of novel Na^+ transport mechanisms. In this work, we report the results of a systematic in-depth investigation of the Na^+ conduction efficiency in novel SPEs prepared by adding different amounts of InAs NWs to a PEO-PVP- NaPF_6 composite polymer.

Single-crystalline InAs NWs of average diameter ~ 40 nm were synthesized by a low-temperature solvothermal method (First step, Fig. 1). Indium trichloride ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$) and arsenic oxide (As_2O_3) were used as the reactants for the InAs NW synthesis. Polyethylene glycol (PEG) and ethylene glycol (EG) were used as solvents. In this growth step, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ was used as the

source for In and As_2O_3 as the source for As for the synthesis of InAs NWs. To prepare the growth solution, 200 mg As_2O_3 and 400 mg $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ were dissolved in a mixture of 100 ml PEG and 50 ml EG and heated to 130 °C with continuous stirring for 30 minutes. Subsequently, a stock solution containing 300 mg sodium borohydride (NaBH_4) dissolved in 10 ml ethylenediamine was mixed with the growth solution. After one hour of reaction, the solution was ultrasonicated and centrifuged in ethanol for 15 to 20 minutes. Finally, high-quality InAs NWs were obtained after drying at 50 °C in vacuum for 24 hours.

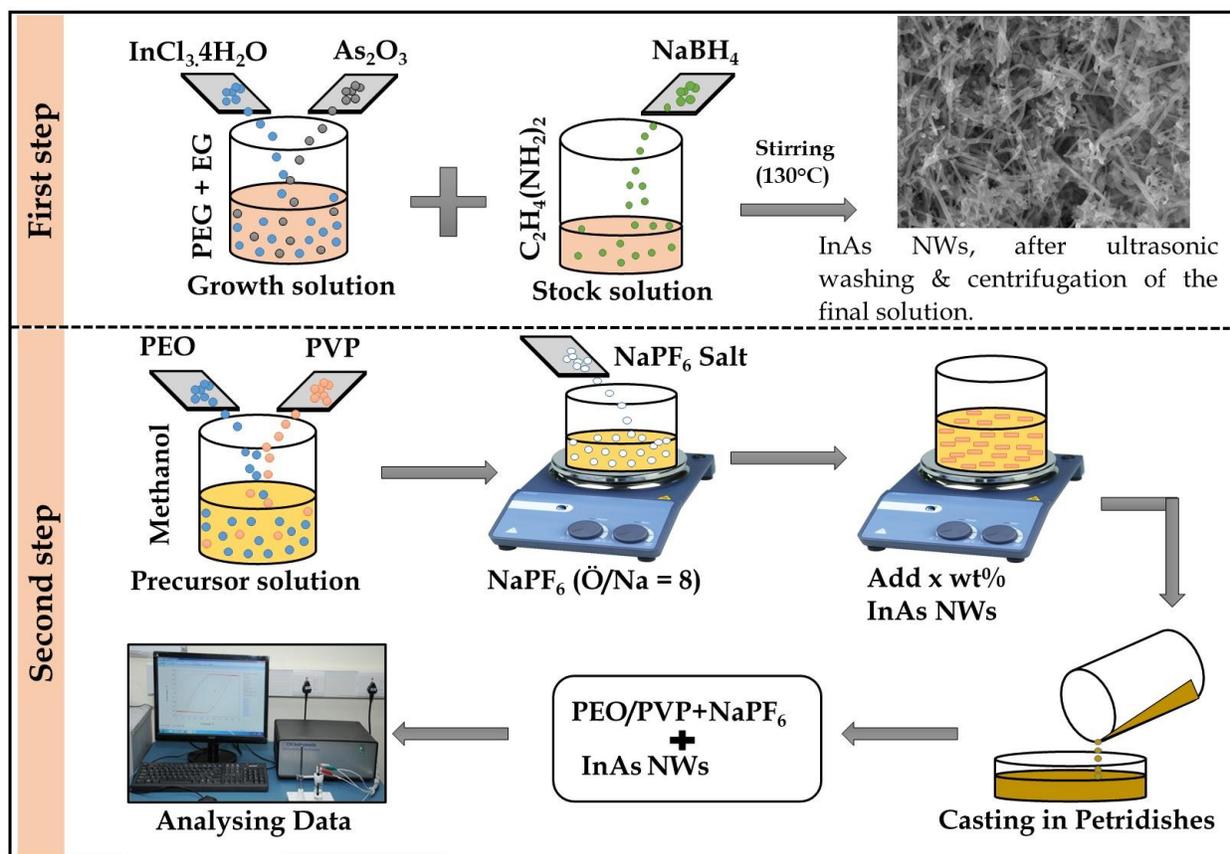


Figure 1: Schematic of the synthesis of InAs NWs and NW-filled composite SPEs.

For fabrication of the SPEs (Second step, Fig. 1), InAs NWs with 0.5–3.0 wt% were added to a methanol solution containing PEO (0.4 g), PVP (0.1 g) and NaPF_6 salt. The molar ratios of O/Na in all the samples were held at 8:1. This mixture was mechanically stirred for 5 h and then

cast into polypropylene Petri dishes. Finally, the InAs NW-filled composite SPE was dried in high vacuum overnight to completely remove all traces of the solvent.

Ionic conductivity is the key parameter for assessing Na⁺ migration efficiency in composite SPEs. Here, this has been investigated with electrochemical impedance spectroscopy (EIS) using two stainless steel blocking electrodes. The Nyquist plots (frequency range 1 Hz to 1 MHz) recorded at 40 °C of the composite SPEs with different InAs NW content (% by weight) are shown in Fig. 2. The appearance of a well-defined semicircle at high frequencies in SPEs without InAs NWs can be attributed to a combination of bulk resistance and bulk capacitance in parallel, originating in the migration of ions and polymer chains. The intercept of the semicircle with the Z' axis yields the bulk resistance. The inset of Fig. 2 shows a typical impedance spectrum for an SPE without InAs NWs. Interestingly, Fig. 2 shows that by adding 0.5 wt% InAs NWs to the SPE the bulk resistance decreases from 40 kΩ to 2 kΩ, decreasing further to 440 Ω in an SPE with 1.0 wt% InAs NWs. It should be noted that a semicircle was not observed for the SPE with 1.0 wt% InAs NWs. This shows that there is a negligible charge transfer resistance, which in turn implies a kinetically fast electrochemical system. The sharp dip corresponds to the double layer capacitance formed at the interface between the electrodes and solid electrolyte. The

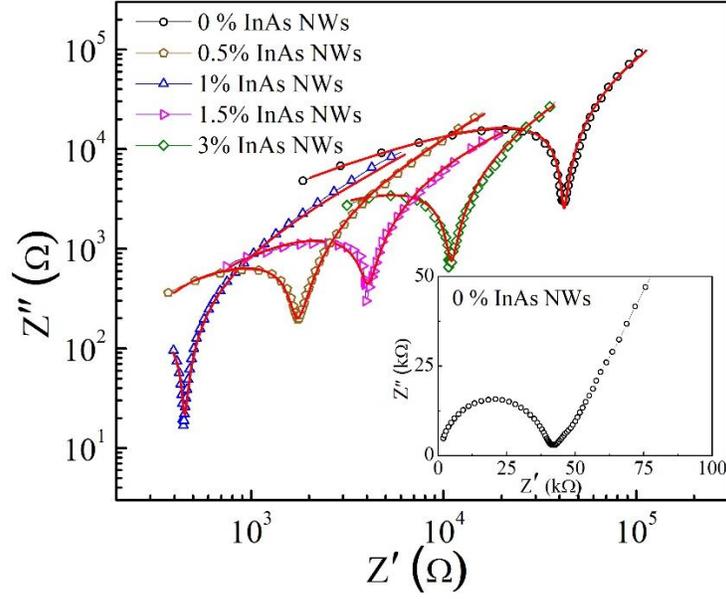


Figure 2: Impedance spectra of the investigated composite PEO-PVP-NaPF₆ SPEs filled with InAs NWs plotted on a double logarithmic scale. The inset shows an impedance spectrum for the SPE without InAs NWs on a linear scale. The red lines are simulated admittance fits to the experimental data.

temperature-dependent ionic conductivity of the different electrolytes, σ , can be extracted from the corresponding bulk resistance R_b using the equation:

$$\sigma = \frac{t}{R_b A}, \quad (1)$$

where t is the thickness of the SPE, and A is the effective area of the blocking electrode. The temperature dependence of the ionic conductivity of the SPEs studied is shown in Fig. 3(a). The composite electrolyte containing 1.0 wt% InAs NWs displayed the highest conductivity of $1.50 \times 10^{-4} \text{ Scm}^{-1}$ at 40 °C, about three orders of magnitude higher than that of the SPE without NWs and to the best of our knowledge the highest reported conductivity of any comparable SPE to date for Na ion battery. Figure 3(b) shows temperature-dependent impedance spectra for the SPE doped with 1.0 wt% InAs NWs. The relationship between ionic conductivity and temperature for an SPE is typically interpreted in terms of Arrhenius-type hopping processes in conjunction with segmental

polymer chain motion described by the Vogel-Tammann-Fulcher (VTF) model [22,26]. Figure 3(a) reveals two different conductivity regimes for the polymer without NWs. At temperatures well below the melting point both crystalline and amorphous phases co-exist, while the amorphous phase dominates at temperatures above the melting temperature. After addition of 1.0 wt% InAs NWs, the temperature dependence of the conductivity changes to a typical Arrhenius relation over the full temperature range:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{RT}\right), \quad (2)$$

with an activation energy E_a of about 50 kJmol^{-1} . Moreover, the preexponential factor in Eqn. 2 increases significantly after the addition of NWs, which leads to an overall strongly enhanced conductivity. A deeper discussion of the interpretation of the large variation in activation energy and can be found below.

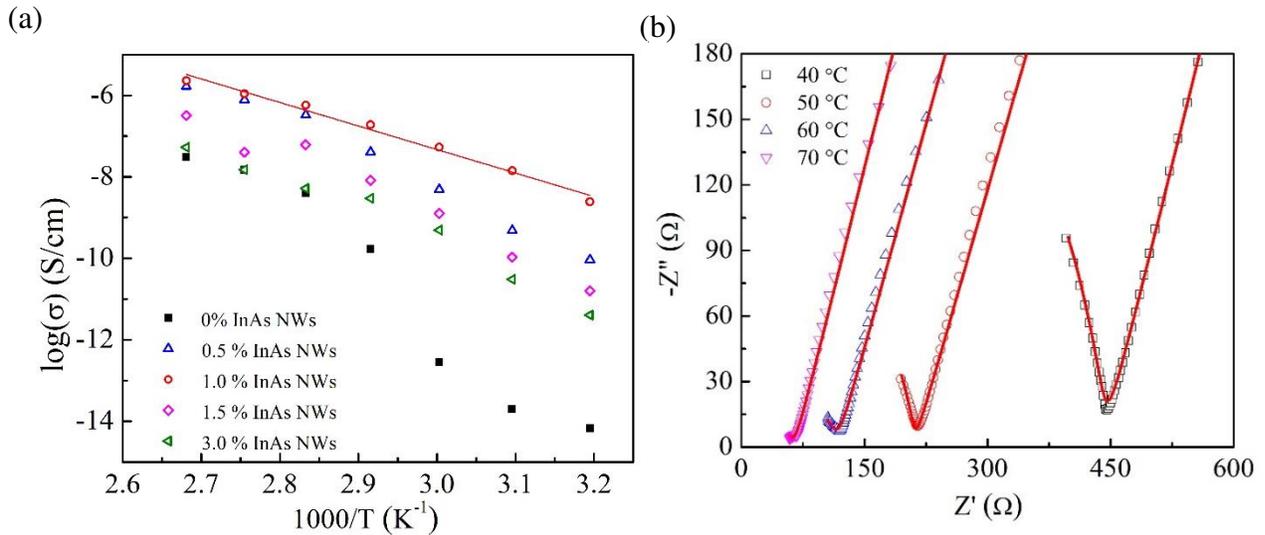


Figure 3 (a) Arrhenius plots of the extracted ionic conductivity of the SPEs. (b) Impedance spectra at different temperatures for the SPE with 1.0 wt% InAs NWs. The red solid lines are simulated admittance fits to the experimental spectra.

As already mentioned, one explanation for the reported enhanced conductivity of SPEs with the addition of nanofillers is a reduction in polymer crystallinity and an increase in the flexible local chains in the amorphous phase [7]. This explanation is in agreement with Fig. 3(a). Figure 4 (a) shows room-temperature X-ray diffraction (XRD) patterns for PEO-PVP- NaPF_6 SPEs without InAs NWs and filled with 1.0 wt% InAs NWs, respectively. The strong signals at around 19° and 23.5° are attributed to the characteristic diffraction peaks from the (120) and (112) planes of semi-crystalline PEO [27].

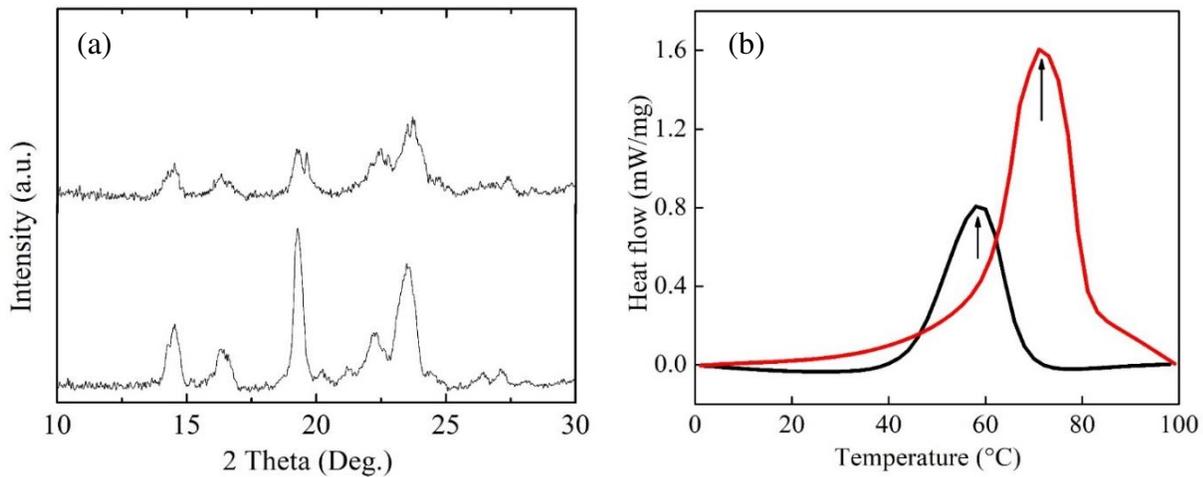


Figure 4: (a) XRD patterns for $(\text{PEO-PVP})_8+\text{NaPF}_6$ SPEs without (lower trace) and with 1.0 wt% InAs NWs (upper trace). (b) Corresponding DSC curves for SPE films with 1.0 wt% InAs NWs (black trace) and without NWs (red trace). The arrows indicate the respective melting temperature.

The relative intensities of these two peaks decrease in the SPE without InAs NWs. This strongly indicates that the added InAs NWs do indeed play the important role of plasticizing the polymer chain and reducing the crystallinity of the PEO. Furthermore, Fig. 4 (a) shows that the typical diffraction peaks near 20° and 22° reported for NaPF_6 [11] are absent in all SPE films, indicating that no agglomerated salt particles exist in the composite electrolytes. The broad peak around 22° ,

and other additional peaks in Fig. 4 (a), are attributed to the formation of complexes between NaPF₆ and PEO-PVP.

To confirm that the InAs NWs reduce the crystallinity of the SPE, differential scanning calorimeter (DSC) curves were recorded (Fig. 4(b)) for PEO-PVP-NaPF₆ films without InAs NWs and with 1.0 wt % InAs NWs. The observed peaks are attributed to the melting point of the corresponding SPE. As is readily observed, the melting point of the bare PEO-PVP-NaPF₆ SPE is around 71 °C, which reduces to about 58 °C after addition of 1.0 wt% InAs NWs. The degree of crystallinity (χ_c) of the SPEs can be assessed by the formula[28]

$$\chi_c = \frac{\Delta H_m}{\Delta H_{PEO}} \times 100\%, \quad (\text{Equation 3})$$

Where ΔH_m is the melting enthalpy of the SPE and ΔH_{PEO} (203 Jg⁻¹) is the melting enthalpy of 100% crystalline PEO [29]. The value of χ_c decreases from 35.6% to 17.8% after the addition of InAs NWs, which shows that the added NWs do indeed decrease the crystallinity of PEO and thereby increase the PEO segmental mobility.

From the experimental results presented so far, it can be concluded that adding InAs NWs to the SPE decreases its crystallinity and so promotes the migration of Na⁺ ions through enhanced PEO segmental mobility. To explain the drastic improvement of ionic conductivity by nearly three orders of magnitude, we propose that two-phase interfacial (PEO-NaPF₆ and InAs NW) Na⁺ transport pathways may play a much greater role in enhancing the ionic conductivity of composite SPEs than has been discussed to date.

In the standard transport model for PEO-PVP-based polymer electrolytes, Na⁺ diffuses in the amorphous phase with the assistance of mobile PEO chain segments. This can be understood in terms of an interaction between the Na⁺ and the electron-rich oxygen groups in PEO. A strong reduction in ionic conductivity was observed below 70 °C in Fig. 3(a) for the bare PEO-PVP-

NaPF₆ SPE. This is consistent with the observed phase transition at 71 °C in Fig. 4(b), where a recrystallization of PEO is expected to reduce segmental motion and the mobility of the Na⁺ ions below the melting point. Adding InAs NWs to the SPE reduces the melting point (Fig. 4(b)) and the activation energy (Fig. 3(a)), indicating that the addition of NWs makes the polymer chains more flexible, resulting in faster segmental motion and an increase in conductivity. Interestingly, adding InAs NWs not only changes the activation energy in Eqn. 2, but also dramatically increases the pre-exponential factor σ_0 over the whole temperature range, implying a dominant conduction mechanism different from random-walk diffusion of Na⁺ through the amorphous PEO. According to the Lewis acid–base theory for inorganic nanoparticle-filled SPEs, it is well known that the concentration and mobility of free Na⁺ play a crucial role in the ionic transport properties [30]. It has also been known for a long time that InAs surfaces and interfaces exhibit an electron accumulation layer in the near-interface region due to defect states which pin the Fermi level far above the conduction band edge [31]. It can thus be expected that the negatively-charged surface of the embedded InAs NWs in the present SPEs both promotes dissociation of contact ion-pairs and provides a fast pathway for Na⁺ diffusion via hopping from one negatively charged site to the next, leading to an increased ion mobility. We therefore propose that the observed drastic conductivity enhancement in InAs NW-filled (PEO-PVP)₈+NaPF₆ composite SPEs is mainly due to the formation of a hitherto unrevealed fast-conductive network induced by the unique NW surface morphology. Interestingly, the conductivity of the SPEs reaches a maximum at 1.0 wt% InAs, after which it drops with increasing InAs NW content, showing a percolation behaviour. This reduction in conductivity is attributed to the formation of effective Na⁺ traps in SPEs with the largest number of percolating pathways, i.e. with largest NW filling. For example, nanowires oriented parallel to the surfaces of the stainless steel electrodes could serve as effective Na⁺ traps

since they restrict the ion motion normal to the electrode material, and hence decrease the conductivity.

Besides exhibiting record-high Na^+ conductivity, the InAs NW-filled composite SPEs also demonstrate significantly better electrochemical stability compared to SPEs without NWs. The electrochemical stability window (ESW) of an electrolyte is the voltage range between which the electrolyte is neither oxidized nor reduced. The ESW is one of the most important characteristics to be identified for solvents and electrolytes used in electrochemical applications. The ESW for SPEs is often determined by the linear sweep voltammetry technique for the cell configuration SS|SPE|SS, where SS refers to stainless steel electrodes. The ESW for PEO-PVP- NaPF_6 SPEs with dispersed InAs NWs was found to be 4.10 V (at 40°C) as shown in Fig.5 (a), which is sufficient for applications in high-performance energy storage devices.

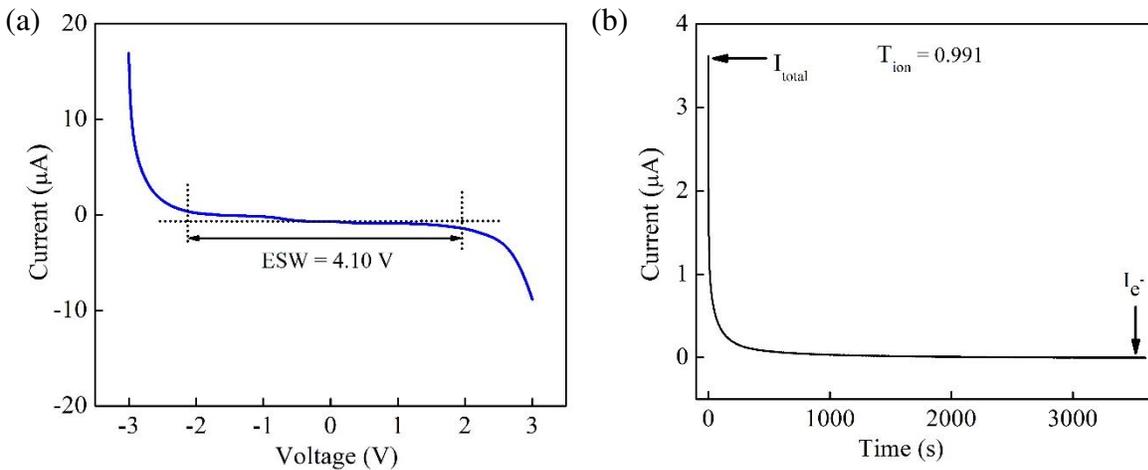


Figure 5 : (a) Linear sweep voltammetry of the SS|(PEO-PVP)₈+NaPF₆|SS cell with 1.0 wt% InAs NWs. (b) Polarization current versus time for the cell in (a).

In order to study the electronic and ionic contributions to the conductivity separately, we performed a transference number measurement. Figure 5(b) shows the plot of the polarization current versus time for the cell in Fig. 5(a) at 40 °C. The large polarization current in the early

phase is due to both Na⁺ and electron transport. The current then starts to decrease rapidly with time as the stainless steel electrode blocks the ions and only allows electrons to pass. Finally, a steady-state condition is reached because of the cell polarization. To distinguish ionic from electronic transport contributions, we have calculated the ion transference number using the relation

$$T_{ion} = \frac{I_T - I_{e^-}}{I_T}, \quad (\text{Equation 4})$$

where I_{e^-} is the electron current, and I_T is the total current due to both electrons and ions. The obtained ion transference number is very close to unity (0.991) in the early phase for the studied composite SPE film. It confirms that the conductivity is mainly due to ions in agreement with the results above suggesting an effective conductive percolating network where Na⁺ hop between negatively charged defect states at the surface of the InAs NWs.

In conclusion, novel composite PEO-PVP-NaPF₆ SPEs with InAs NWs have successfully been prepared by a cheap, low-temperature, solvothermal method. Temperature-dependent Na⁺ conductivity measurements reveal a superior conductivity of $1.5 \times 10^{-4} \text{ Scm}^{-1}$ and an electrochemical stability window of 4.10 V @ 40 °C for a composite electrolyte with 1.0 wt% InAs NWs. In order to explain the excellent characteristics, we propose a new transport model where the migration of Na⁺ is strongly enhanced by hopping between nearby negatively charged defect sites present on the surface of the InAs nanowires forming an effective complex conductive percolation network. Our work represents a significant advancement in the development of novel SPEs with embedded engineered ultrafast 1D percolation networks for the next-coming generation of low-cost high-performance sodium-ion batteries.

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Acknowledgments

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Figures

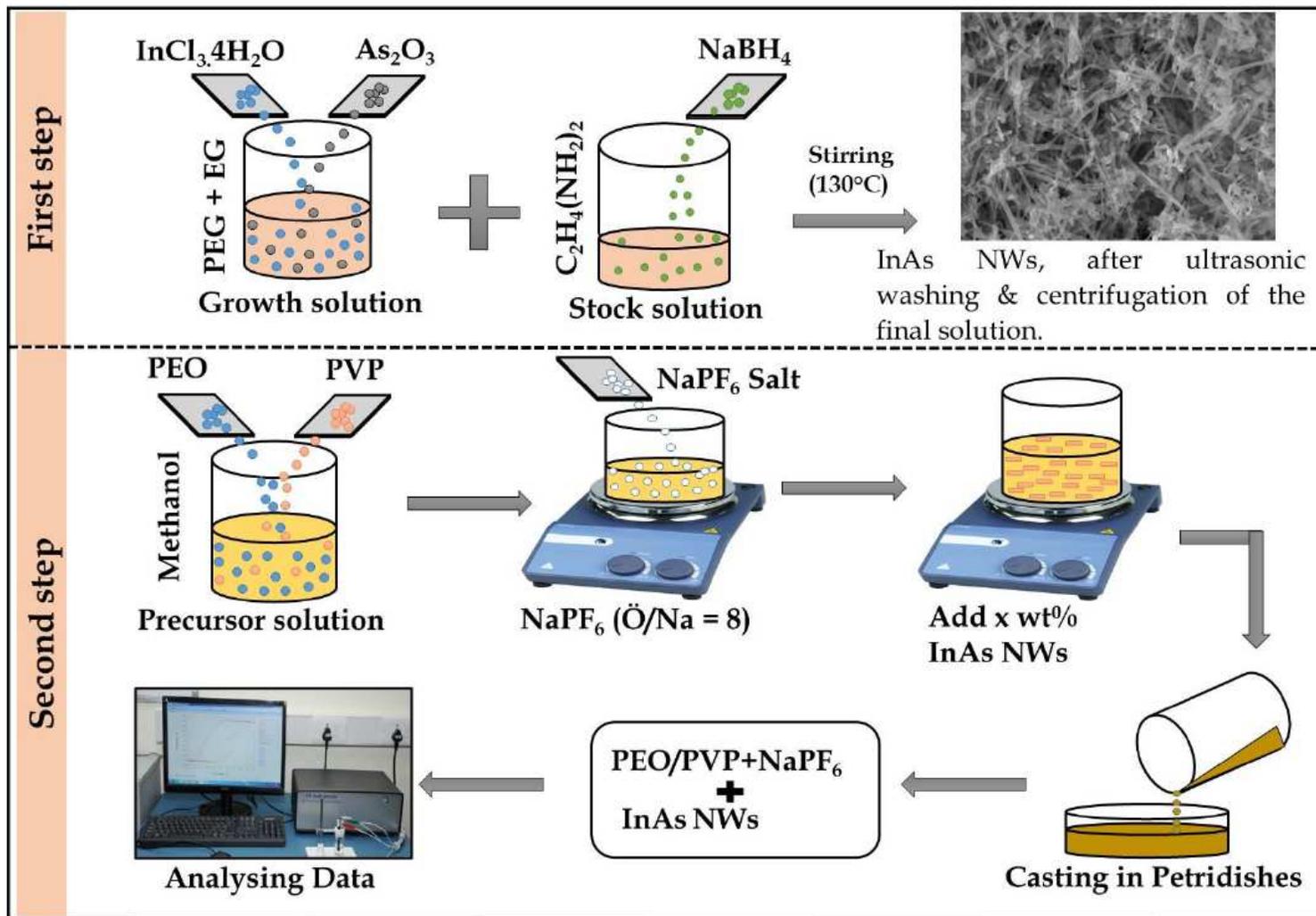


Figure 1

Schematic of the synthesis of InAs NWs and NW-filled composite SPEs.

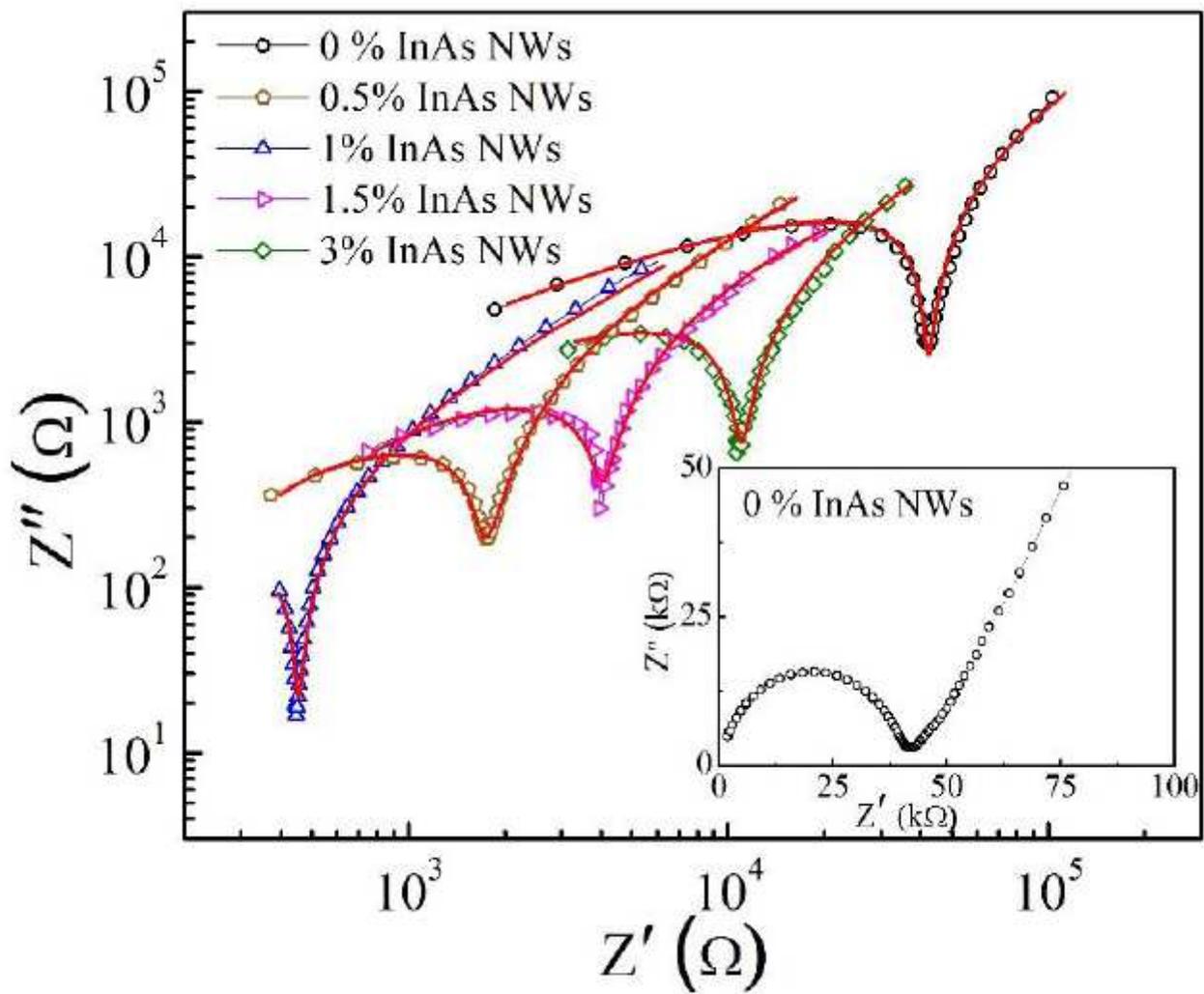


Figure 2

Impedance spectra of the investigated composite PEO-PVP-NaPF6 SPEs filled with InAs NWs plotted on a double logarithmic scale. The inset shows an impedance spectrum for the SPE without InAs NWs on a linear scale. The red lines are simulated admittance fits to the experimental data.

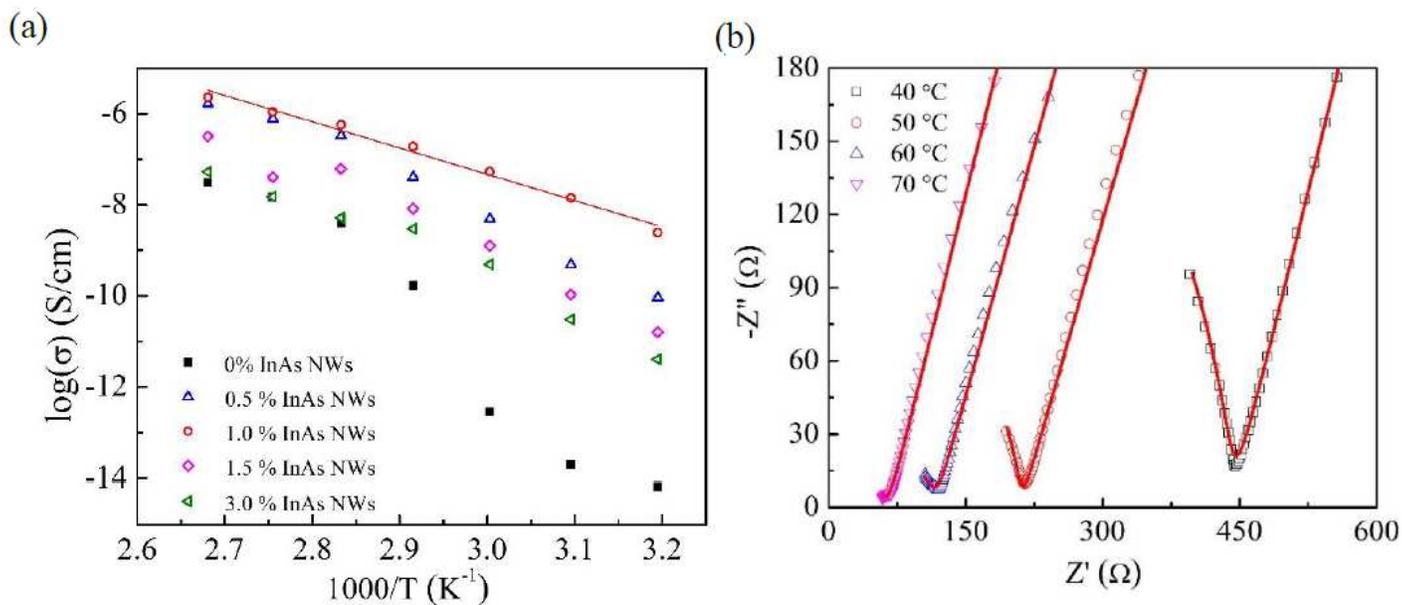


Figure 3

(a) Arrhenius plots of the extracted ionic conductivity of the SPEs. (b) Impedance spectra at different temperatures for the SPE with 1.0 wt% InAs NWs. The red solid lines are simulated admittance fits to the experimental spectra.

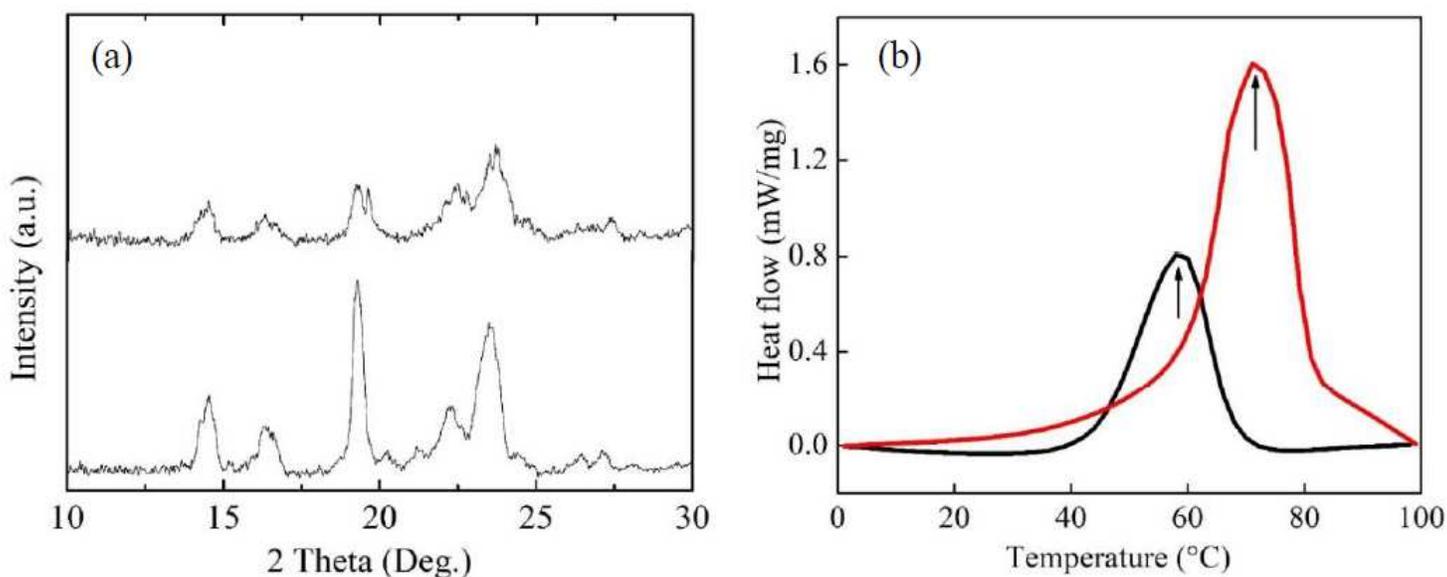


Figure 4

(a) XRD patterns for (PEO-PVP)₈+NaPF₆ SPEs without (lower trace) and with 1.0 wt% InAs NWs (upper trace). (b) Corresponding DSC curves for SPE films with 1.0 wt% InAs NWs (black trace) and without NWs (red trace). The arrows indicate the respective melting temperature.

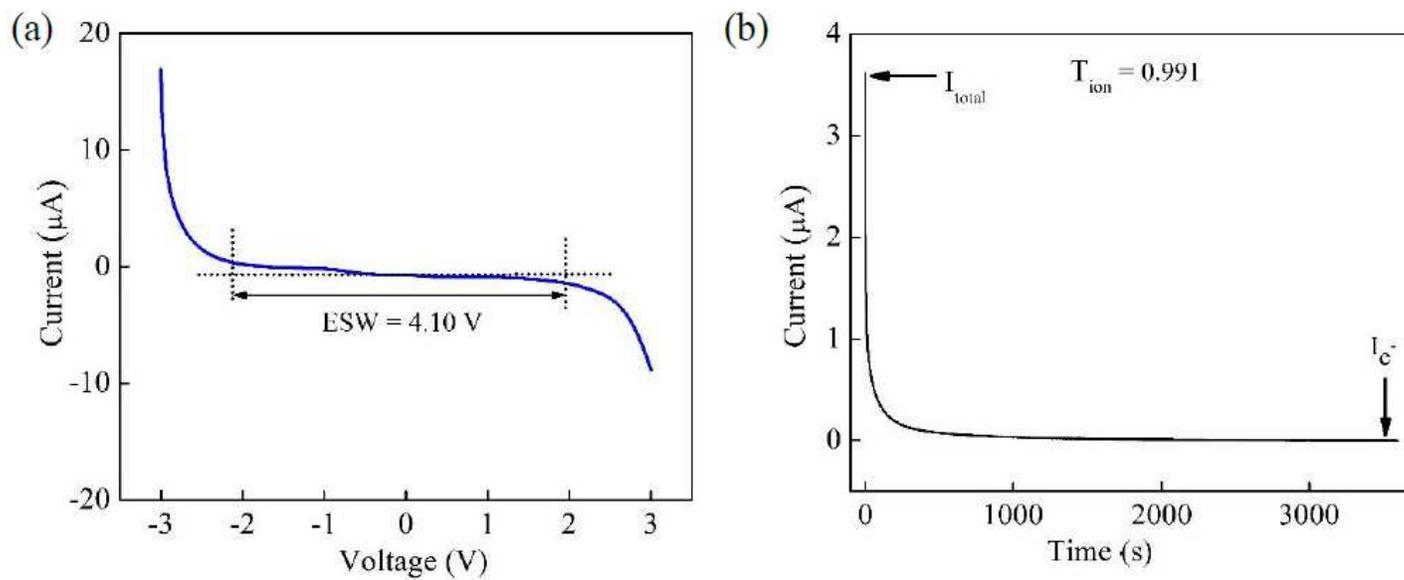


Figure 5

(a) Linear sweep voltammetry of the SS|(PEO-PVP)8+NaPF₆|SS cell with 1.0 wt% InAs NWs. (b) Polarization current versus time for the cell in (a).