

**Synthesis and Optimization of Poly(Nickel-Ethylenetetraathiolate)  
for High Performance n-Type Thermoelectric Polymers**

A Thesis Presented to The Academic Faculty

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In Partial Fulfillment

of the Requirements for the Research Option in the  
George W. Woodruff School of Mechanical Engineering

Georgia Institute of Technology

May 2017

# **Synthesis and Optimization of Poly(Nickel-Ethylenetetraathiolate)**

## **for High Performance n-Type Thermoelectric Polymers**

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## I. INTRODUCTION

The desire for low cost, lightweight, and flexible power generation has drawn attention to the prospects of using organic thermoelectrics for energy harvesting.<sup>1-6</sup> The efficiency of a thermoelectric material to convert heat into electricity is determined by the non-dimensional figure of merit,  $zT$ , which comprises the material's electrical conductivity ( $\sigma$ ), thermal conductivity ( $\kappa$ ), and Seebeck coefficient ( $S$ ) in the form of  $zT = S^2\sigma T/\kappa$ , where  $T$  is the absolute temperature.<sup>1-2</sup> Conventional thermoelectrics include inorganic materials such as bismuth telluride and lead-based chalcogenides and skutterudites that are suitable for low ( $< 200$  °C) and high temperature ( $> 500$  °C) applications, respectively. Additionally, these materials are not widely abundant and are complex to process,<sup>7-9</sup> which in turn limits their scalability and also increases their cost significantly. For low temperature applications, electrically conducting polymers compete directly with inorganics with advantages due to their flexibility, low density, and abundance.<sup>2,6</sup> Furthermore, the thermoelectric properties of organic materials can be tuned via molecular modification, which enables decoupling of  $S$  and  $\sigma$ ; normally electrical conductivity increases while the Seebeck coefficient decreases with increasing charge carriers.<sup>10</sup> The additions of dopants and molecular modification have been demonstrated to increase both properties at the same time or, at least, increase one property without negatively affecting the other.<sup>10-11</sup> Combined with their inherent low thermal conductivity below 0.3 W/m-K, polymer materials could be a viable option for thermoelectric generators.<sup>2, 12-13</sup>

In the past decade, efforts have been made to improve the thermoelectric properties of organic materials to match their inorganic counterparts.<sup>14-28</sup> Significant progress has been made with p-type polymers;<sup>14-19</sup> a prime example is DMSO de-doped PEDOT:PSS that has a reported  $zT$  of 0.42 and a power factor (defined as  $S^2\sigma$ ) of 469  $\mu\text{W}/\text{m-K}$ .<sup>219</sup> However, n-type materials have lagged behind due to their

instability in air.<sup>20-28</sup> Some of the highest performing n-type polymer TEs include poly[K<sub>x</sub>(Ni-ett)],<sup>25</sup> CoCp<sub>2</sub> encapsulated with SWNTs,<sup>29</sup> and potassium-doped C<sub>70</sub>,<sup>26</sup> with power factors of 66, 12, and 28 μW/m-K<sup>2</sup>, respectively. However, these materials are processed through compression (pellets), filter cake collection, and sublimation.<sup>24, 26, 29</sup> These processing methods are less cost-effective than the high-throughput of solution processing.<sup>1, 6, 30-31</sup>

Considerable efforts have been made to improve the thermoelectric properties of solution processible n-type polymers. This includes blending poly[Ni-1,1,2,2-ethylenetetra-thiolate] with PVDF/DMSO to form a composite that has a power factor of 0.43 μW/m-K<sup>2</sup>,<sup>32</sup> this is much lower than the 66 μW/m-K power factor found in the compressed poly[K<sub>x</sub>(Ni-ett)] pellet.<sup>25</sup> Other solution processible n-type polymers, include P(NDIOD-T2), which has a power factor of 0.6 μW/m-K<sup>2</sup> through addition of suitable dopants<sup>33</sup>, and self-doped, water soluble perylene diimides, which have a power factor up to 1.4 μW/m-K<sup>2</sup> through molecular modification.<sup>11</sup> More recently, Shi *et al.* reported the highest power factor for a solution processed n-type material of 28 μW/m-K<sup>2</sup> by modifying the polymer backbone of BDPPV.<sup>34</sup> Although N-DMBI doped FBDPPV is currently the highest performing solution processed n-type polymer, it is difficult to synthesize at a large scale. The synthesis of FBDPPV involves several steps and requires microwave heating, which could complicate scale-up.<sup>35</sup> In contrast, ethylenetetra-thiolate polymers involve a facile synthesis that is easily scaled up while having a potentially high power factor.<sup>32</sup> The combination of high performance and scalability could make ethylenetetra-thiolate polymers the ideal candidate for implementing conducting polymers with thermoelectric applications.

### ***Fundamentals and Applications of Thermoelectrics***

Thermoelectricity manifests in three effects, the Seebeck, Peltier, and Thomson effects, though the underlying physical origin of these effects is the same and describes the interplay between heat and

electricity.<sup>1</sup> The Seebeck effect describes the direct conversion of a temperature difference into a voltage difference. The maximum efficiency of thermal to electrical energy conversion,  $\eta_P$  can be expressed as:<sup>36</sup>

$$\eta_P = \frac{T_h - T_c}{T_h} \left[ \frac{\sqrt{1 + zT_{ave}} - 1}{\sqrt{1 + zT_{ave} + \frac{T_c}{T_h}}} \right]. \quad (1)$$

$T_h$  and  $T_c$  represent the hot and cold temperatures respectively, while  $zT_{ave}$  represents the average  $zT$  over that temperature range. The  $zT$  represents the figure-of-merit of a material and is given by:<sup>1</sup>

$$zT = \frac{S^2 \sigma}{\kappa} T, \quad (2)$$

where  $S$ ,  $\sigma$ , and  $\kappa$  represent the material properties Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. The absolute temperature is represented by  $T$ . The Seebeck coefficient describes the voltage produced when a temperature difference is applied across a material and can be positive or negative.<sup>1</sup> For a  $zT$  of 1, and  $T_c=273$  K, and  $T_h=373$  K, the conversion efficiency is  $\sim 5\%$ .<sup>1,37</sup>

Inorganic materials were the first class of thermoelectric materials found to be of practical use. Generally, inorganic thermoelectric materials have high electrical conductivity, high Seebeck coefficients, and are suitable for high temperature applications where the thermal conductivity is lower. Inorganic materials have had the earliest commercial success due to their high performance with  $zT$  at or above 1 slightly above room temperature. Different inorganic materials exhibit high  $zT$  across a wide range of temperatures. Bismuth containing chalcogenides have shown  $zT > 1$  at room temperature,<sup>9</sup> while skutterudites have shown  $zT$  of 1.4 at 873 K.<sup>38</sup> Despite high performance, the environmental toxicity, scaling difficulties, and costly processing associated with inorganic materials limit the number of avenues for successful applications that could use thermoelectrics.

Inorganic materials have found a variety of niche applications.<sup>39</sup> Thermoelectrics have been used in deep-space missions in radioisotope thermoelectric generators. By combining a thermoelectric generator with a highly active radioisotope as the heat source, long duration, deep-spacecraft were

realized.<sup>40</sup> Inorganic thermoelectric materials are also used as Peltier coolers for microprocessor electronic cooling and refrigeration applications.<sup>39</sup> While thermoelectric cooling has found success in several novelty cooling applications where ice-free, quiet, and vibration-free features are desired<sup>39</sup>, these devices cannot match the efficiency and performance of compressor-based coolers.<sup>37</sup>

Currently, thermoelectric applications are limited by performance and cost. The current  $zT$  available makes thermoelectrics impractical for a variety of potential applications. At  $zT = 2$ , thermoelectrics could become applicable for heat pumping and air-cooling systems.<sup>39</sup> The solid-state functionality would remove the need for refrigerants, thus eliminating the consequence of green-house gas emissions from refrigerant leakage.<sup>39</sup> Also at  $zT = 2$ , waste heat recovery to electricity becomes acceptable in vehicle exhaust, industrial applications, and replacements for small internal combustion engines.<sup>39,41</sup> While inorganic materials are closest to the  $zT = 2$  goal, cost in material and processing could limit their potential for wide-spread adoption.<sup>7-9</sup> Organic thermoelectric materials could potentially eliminate these problems due to high carbon abundance and potential for solution processibility.<sup>6</sup>

### ***A New Direction in Application with Organic Thermoelectrics***

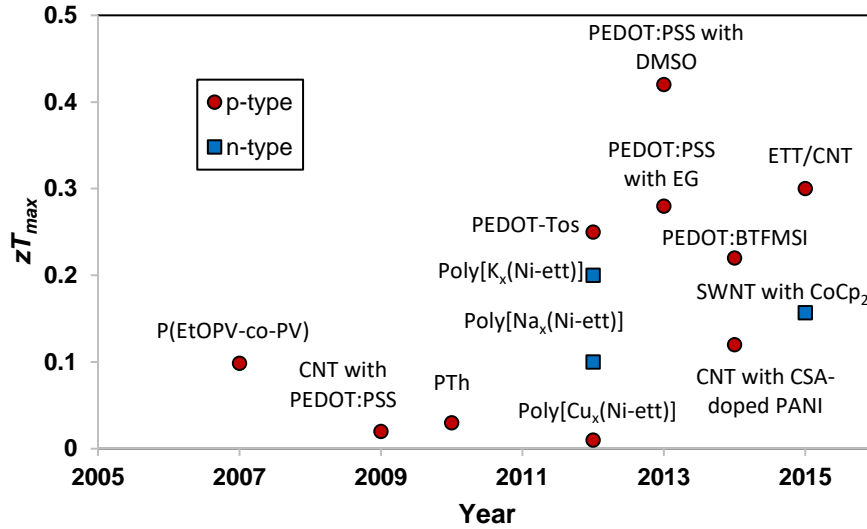
The emergence of conducting polymers offers an alternative to inorganic thermoelectric materials. Polymers are long chain molecules of repeating units that are produced when monomers are polymerized. A common feature of conductive polymers is that the backbone of the polymer is  $sp^2$  hybridized and conjugated throughout. This allows charge to conduct through a polymeric material.<sup>1</sup> Polymer properties can also be tuned in a variety of ways such as side-chain modification and doping. Molecular modification of the side-chains allows conductivity and other properties to be manipulated before the polymerization. Doping, defined broadly as the introduction of another molecule to a material, can be used to modify the properties of polymers after polymerization.

Organic-based materials offer many advantages that make these materials potentially competitive to inorganic materials. Polymers generally have lower thermal conductivity often near  $\sim 0.25$  W/m-K.<sup>1</sup> For polymers this means the focus is not on  $zT$  but rather on the power factor, PF, which is related to the numerator of the  $zT$  equation, as:<sup>1,42</sup>

$$PF = S^2\sigma, \quad (3)$$

The constant low thermal conductivity allows researchers to focus primarily on increasing the power factor using various techniques such as molecular modification or doping as described above. Unlike inorganic materials, organic materials are also often soluble in common solvents allowing for solution processing.<sup>1</sup> Common solution processing methods include spin-coating, drop casting, dip coating, and inkjet printing. These solution processing methods allow facile fabrication of flexible thin-films, which can open new engineering possibilities such as wearable electronics.<sup>1</sup>

Organic thermoelectric materials have a wide variety of features that make them attractive, but thermoelectric performance is considerably lower than seen in inorganic thermoelectric materials. Until recently, almost all organic thermoelectric materials showed  $zT < 0.1$ .<sup>42</sup> However, recent advances in organic electronics has accelerated the increase in  $zT$  as shown in Figure 1.<sup>43</sup> Organic materials are quickly approaching the same  $zT$  found in inorganic materials and  $zT$  required for desired applications. While there are many p-type organic materials with  $zT > 0.1$ , development of n-type materials has not met the same level of success. Because many n-type organic materials are air-sensitive, there are only a select few n-type materials that are both air-stable and have a  $zT > 0.1$ . Table 1 lists several different n-type polymers and their thermoelectric properties.



**Figure 1:** Evolution of the material  $zT$  for polymer TEs in the last decade. Here  $zT_{max}$  is used to represent the highest  $zT$  value reported. [PANI = polyaniline; PEDOT-Tos = poly(3,4-ethylenedioxythiophene)-tosylate; SWNT = single-walled nanotube; CoCp<sub>2</sub> = cobaltocene; CSA = camphor sulfonic acid; EG = ethylene glycol; P(EtOPV-co-PV) = phenylenevinylene copolymer with diethoxyphenylene; PTh = polythiophene; BTFSI = bis(trifluoromethylsulfonyl)imid]. Figure adopted from Ref. <sup>43</sup>

**Table 1:** Thermoelectric properties of n-type polymers.

Polymer	$S$ ( $\mu\text{V/K}$ )	$\sigma$ (S/cm)	PF ( $\mu\text{W/m-K}^2$ )	$T$ (K)	Ref.
Poly(Ni-ett) films from potentiostatic deposition	-90-140	200-400	453	300	44
Poly(Ni-ett) from potentiostatic deposition	-139.6	67.5	131.6	360	45
CoCp <sub>2</sub> encapsulated with SWNTs Film	-41.8	432	75.4	320	29
poly[K <sub>x</sub> (Ni-ett)] Pellet	-122	44	66	300	25

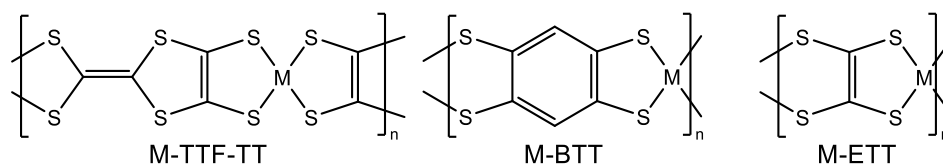


K-doped C <sub>70</sub> Film	-22.5*	550	28	300	<sup>26</sup>
N-DMBI doped FBDPPV Film	-141*	14	28	300	<sup>34</sup>
(tpp)-doped SWNT Film	-73	49.8	27	310	<sup>46</sup>
Cr <sub>2</sub> (hpp) <sub>4</sub> doped C <sub>60</sub> Film	-175	4	12	313	<sup>22</sup>
CuTCNQ blended with F <sub>4</sub> TCNQ Film	-600*	0.07	2.5	370	<sup>47</sup>
Self-doped perylene diimides Film	-167*	0.5	1.4	N/A	<sup>11</sup>
N-DMBI doped P(NDIOD-T2) Film	-850	0.008	0.6	N/A	<sup>33</sup>
poly[K <sub>x</sub> (Ni-ett)]/PVDF Film	-44.9	2.12	0.43	300	<sup>32</sup>

\*Denotes property that was estimated from figures

### High Performance Found in Metal-coordinated ethylenetetrathiolate (ETT) polymers

Thiochelate polymers are polymers with transition metal complexes and sulfur-containing ligands. In these polymers, conjugation is achieved through the  $d\pi$ - $\pi$  bonding between the ligands and transition metal.<sup>48</sup> Figure 2 shows several such polymers. These polymers were first studied in the 1970's for their conductivity as well as their ease of synthesis and stability. Conductivities of up to 50 S cm<sup>-1</sup> at room temperature were observed by substituting the ligand or metal.<sup>49</sup> A common drawback of these one-dimensional conductors were their insoluble nature, which is common among ladder polymers. The insolubility is problematic for processing and purification.<sup>48</sup>

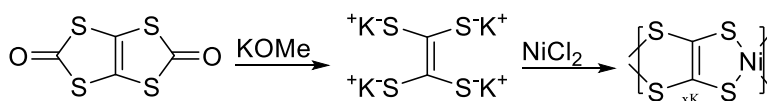


**Figure 2:** Examples of thiochelating polymers:

tetrathiafulvalenetetrathiolate (TTF-TT), benzene-1,2,,4,5-tetrathiolate (BTT), ethylenetetrathiolate (ETT)

These polymers have been studied for over 30 years due to their high electrical conductivity,<sup>50-54</sup> but their thermoelectric potential was first reported by Sun *et al.* in 2012 with the highest n-type power factor of  $66 \mu\text{W}/\text{m}\cdot\text{K}^2$  for poly[ $\text{K}_x(\text{Ni-ett})$ ].<sup>25, 32, 55-57</sup> However, the synthesized polymer is an infusible black powder that does not dissolve in most common solvents.<sup>25</sup> Recent studies have focused on making these polymers amenable to solution processing,<sup>32, 55-56, 58</sup> and Jiao *et al.* formed a composite of poly[ $\text{K}_x(\text{Ni-ett})$ ] powders in polymer suspensions, albeit with a reduced power factor of  $0.43 \mu\text{W}/\text{m}\cdot\text{K}^2$ .<sup>32</sup> Other groups have dispersed ETT nanoparticles in a solvent with significant reductions in electrical conductivity.<sup>58-59</sup> The major challenge has been maintaining high thermoelectric properties while making this polymer solution processible.

Generally, ethylenetetrathiolate polymers are synthesized by reacting 1,3,4,6-tetrathiapentalene-2,5-dione with 4 molar equivalents of an alkali base in an alcohol solvent to produce the ethylene tetrathiolate anion ( $\text{C}_2\text{S}_4^{4-}$ ). Addition of one molar equivalent of transition metal salts and subsequent oxidation results in the formation of the metal-coordinated polymer, as shown in Scheme 1. However, the ethylenetetrathiolate polymers have been found to produce higher performing materials when processed via electrochemical polymerization or potentiostatic deposition.<sup>44-45</sup> A comprehensive literature review of ETTs is presented in Appendix A to facilitate comparison of different synthesis schemes. In conclusion, the wide variety of synthesis and process procedures show that there is an abundance of opportunity to further increase properties in ETTs.



**Scheme 1:** Synthesis of poly[ $\text{K}_x(\text{Ni-ett})$ ] as reported in <sup>25</sup>

In this work, I focus on improving the thermoelectric properties of poly[K<sub>x</sub>(Ni-ett)] by modifying the synthesis, since it is the best performing n-type metal-coordinated polymer. One main observation from Appendix A is that the electrical conductivity depends on the reaction environment (air-free/inert/open to atmosphere) and reaction time (longer time allows the reaction to proceed to completion and results in larger  $\sigma$  values<sup>25</sup>). With this observation, I extend the time for each reaction step to 24 hours and vary the oxidation time in the final step. In addition, I vary the amount of potassium methoxide and nickel chloride in order to test the sensitivity of the final product to the reactants. I report the thermoelectric properties of poly[K<sub>x</sub>(Ni-ett)] thin-film composite under these different reaction conditions in order to obtain a high power factor for a solution processible polymer.

### ***Thesis Question***

The questions that this thesis wants to answer is :

***Can the thermoelectric properties of poly[K<sub>x</sub>(Ni-ett)] films be optimized without compromising scalability or facile manufacturing?***

I attempted to answer this by:

1. Identifying procedures in the synthesis that could be manipulated
2. Optimizing thermoelectric properties by tuning the synthesis variables
3. Maximizing composite thermoelectric properties by varying film composition

## II. METHODS AND MATERIALS

### *Poly[K<sub>x</sub>(Ni-ett)] Synthesis*

First, 1.5 g of potassium methoxide (Alfa Aesar) was dissolved in 45 mL of methanol (BDF, ACS grade) in a 250-mL, round-bottom flask. After the potassium methoxide is fully dissolved, 1 g of 1,3,4,6-tetrathiapentalene-2,5-dione (TCI America) was added to the solution. The mixture was then refluxed at 75 °C for 24 hours. After 24 hours, a previously prepared solution of 0.63 g nickel (II) chloride (Sigma Aldrich) in 25 mL of methanol and 300  $\mu$ L of deionized water was then added to the mixture. The new mixture is then refluxed at 75 °C for an additional 24 hours. After 24 hours, the system was exposed to air for 30 minutes before extraction and vacuum filtration. The filter cake was washed with deionized water and methanol three times with 40 mL of each solvent. Next, the material was dried under vacuum. Finally, the dry powder is then finely grounded with a pestle and mortar.

### *Fabrication of Thermoelectric Thin-films*

First, 40 mg of finely grounded ethylenetetrathiolate is placed in a 2 mL vial with 10 mill zirconia balls. Next, 1 mL of a 10 mg PVDF/mL DMSO solution (previously prepared by dissolving PVDF in DMSO at 80°C for 4 hours) is added to the vial to create a suspension. The suspension is then shaker-milled for 30 minutes at 3000 rpm. 35  $\mu$ L is then dropcasted on previously cleaned 1 cm x 1 cm glass slides (slides were cleaned by sequential ultrasonication in deionized water, acetone, and isopropyl alcohol for 3 minutes each followed by 5 minutes of plasma cleaning). Coated slides are then placed in a vacuum oven and dried for 5 minutes and then heated to 50 °C. Films samples were removed from the oven after out ~20 minutes when the films were dry.

### *Film Measurement of Electrical Conductivity and Seebeck Coefficient*

Dry films had four gold contact pads (~120 nm thick) deposited on the surface in an e-beam evaporator. Electrical conductivity and Seebeck coefficient of the films were measured with an in-house van Der Pauw technique. Films were prepared by applying thermal grease to the backside of the glass

substrate. The thermal grease was used to promote good thermal contact between the glass substrate and Peltier unit. The Seebeck coefficient was also measured in-house using temperature-controlled stages to apply a temperature difference and voltage probes measured the resulting thermoelectric voltage. The temperature-controlled stages were two Peltier units separated by 3 mm and was used to apply a series of temperature differences up to  $\Delta T = 10$  °C. Voltage and temperature data were acquired using a Keithley 2700 DMM with a 7708 Mux card. The acquired data was then used to calculate the Seebeck coefficient by determining the slope from a  $V - \Delta T$  plot. All films were 5-10  $\mu\text{m}$  thick and measured via profilometry.

### III. RESULTS AND DISCUSSION

#### *Optimizing Poly[K<sub>x</sub>(Ni-ett)] Synthesis for Thermoelectric Performance*

Prior to experimentation, I attempted to repeat the synthesis steps described by Sun *et al.*<sup>25</sup> Two alterations were made. At each reaction steps, the material was exposed to open atmosphere and the final reaction step was extended to 24 hours to ensure full oxidation. Figure 3 shows the final product of the synthesis after filtration and vacuum drying. Elemental compositions from combustion analysis is shown in Table 2. Theoretical values are calculated from the atomic weight percentages of the proposed synthesis structure from Scheme 1. The elemental analysis of the material synthesized by Sun *et al.* agrees well with the theoretical structure where potassium content is assumed to be negligible. The material in this work shows a carbon and hydrogen content similar to Sun *et al.*'s work.<sup>25</sup> However, the sulfur content in the material produced in this work is approximately a third less than the theoretical structure.



**Figure 3:** Collected ETT material immediately after filtration.

**Table 2: Elemental analysis of ETT material.**

Elemental Analysis - wt. %			
Element	Theory	Sun <i>et al.</i> <sup>25</sup>	This work
M = Ni	27.82	25.85	-
C	11.39	12.99	10.07
H	0	1.12	1.19
A = K	0	0.57	-
S	60.79	-	39.95

To make films for thermoelectric property testing, the ETT was suspended in a 20 mg PVDF/ mL of DMSO solution as described by Jiao *et al.*<sup>32</sup> ETT was synthesized and made into ETT/PVDF films three times and are represented by synthesis 1-3 in Table 3. The films produced in this work was found to have a consistently higher electrical conductivity and lower Seebeck coefficient than results found in Jiao *et al.* work.<sup>32</sup> The discrepancy could be caused by the differences in synthesis; the scale performed in their work was on the 7 g basis of TPD and my work used 1 g basis of TPD.<sup>32</sup> However, another procedural change in my work includes drop casting the suspension onto a glass substrate instead of printing onto a polyethylene terephthalate substrate. I also heated in vacuum at 50 °C instead of heating for 10 hours at 90 °C.<sup>32</sup> The differences between synthesis 1 and synthesis 2-3 represent the procedural change of solubilizing NiCl<sub>2</sub> by hydration before addition to the reaction mixture. Synthesis 4 represents a scale-up performed on the 5 g basis of TPD, which resulted in properties closer to the values found by Jiao *et al.* work.<sup>32</sup>

**Table 3: Thermoelectric properties of ETT/PVDF Composite films.**

<b>Trial #</b>	<b><math>\sigma</math> (S/cm)</b>	<b><math>S</math> (<math>\mu\text{V}/\text{K}</math>)</b>	<b><math>S^2\sigma</math> (<math>\mu\text{W}/\text{m}\cdot\text{K}^2</math>)</b>
<b>Jiao <i>et al.</i><sup>32</sup></b>	2.12	-45*	0.43
<b>Synthesis 1</b>	$2.95 \pm 0.06$	$-24.82 \pm 1.09$	0.18
<b>Synthesis 2</b>	$4.97 \pm 0.04$	$-26.08 \pm 0.71$	0.34
<b>Synthesis 3</b>	$5.19 \pm 0.07$	$-25.98 \pm 0.77$	0.35
<b>Synthesis 4</b>	$2.33 \pm 0.05$	$-37.49 \pm 0.67$	0.33

\* In this work, the Supplemental Information reports this value as  $-28 \mu\text{V}/\text{K}$  where the main manuscript reports this value as  $-45 \mu\text{V}/\text{K}$ . It is unclear which value is correct.

Synthetic changes were then performed to investigate the link between synthesis and thermoelectric performance. Table 4 shows four synthesis where variations in both potassium methoxide and nickel chloride were incorporated into the synthesis. In Table 2, Sun *et al.* show that only a trace amount of potassium is retained in the product, which suggests that the potassium methoxide is only used to generate and stabilize the ethylene-tetrathiolate anion. Two synthesis varying potassium methoxide, one with half and one with double the amount, were performed. These changes were shown to negatively affect the thermoelectric properties. Half of the required potassium methoxide was shown to decrease the Seebeck coefficient by two-thirds. The reduction in the Seebeck coefficient may be due to the insufficient potassium ions needed to generate the ethylene-tetrathiolate anion from the monomer in the first reaction step. Double the required potassium methoxide was shown to significantly reduce electrical conductivity. The reduction in conductivity could be a result of the excess potassium methoxide participating in unwanted reactions; Potassium methoxide is known to react with nickel chloride.<sup>60</sup> Consumption of nickel through other reactions could negatively affect the material's ability to build molecular weight and thus impact properties.

Next, nickel concentrations were investigated by reducing and increasing addition of nickel chloride. Sun *et al.* reported that the alkali ions compete with the metal ions where poly[ $\text{Ni}_x(\text{Ni-ett})$ ] is



produced in the presences of excess nickel.<sup>25</sup> They report that the pellet of poly[Ni<sub>x</sub>(Ni-ett)] performs at about 1/5 and 1/14 of the reported power factor of the poly[Na(Ni-ett)] and poly[K(Ni-ett)], respectively. My work expands on the investigation by performing two syntheses with 20 % less or 20 % more nickel chloride than the usual synthesis. Nickel chloride addition was reduced by 20% to lower the competition between the alkali and nickel cations but high-quality films were unable to be produced. A synthesis of 20% excess nickel chloride was conducted and produced films that exhibited slightly higher performance compared to material produced from equimolar concentrations of nickel chloride and ethylenetetrathiolate monomer.

**Table 4:** Variations in the reactant concentrations.

<b>Trial #</b>	<b><math>\sigma</math> (S/cm)</b>	<b><math>S</math> (<math>\mu</math>V/K)</b>	<b><math>S^2\sigma</math> (<math>\mu</math>W/m-K<sup>2</sup>)</b>
<b>Half KOMe</b>	4.68 $\pm$ 0.24	-12.32 $\pm$ 0.75	0.07
<b>Double KOMe</b>	<1	-29.45 $\pm$ 2.03	<0.01
<b>-20%Nickel Salt</b>	N/A	N/A	N/A
<b>+20% Nickel Salt</b>	4.77 $\pm$ 0.25	-28.86 $\pm$ 0.28	0.40

In addition to changing reagent concentrations, I also explored changing some of the synthesis procedures. A high pressure and high temperature synthesis was performed in a sealed vessel at approximately 125 °C as shown in Figure 5. The synthesis exhibited higher performance, as shown in Table 5, but it was inconclusive if the increased performance was due to changes in reaction conditions or vessel shape. A synthesis was performed with the addition of tetrathiafulvalene monomer to increase conductivity in the form of a new copolymer. The compressed pellets of pure tetrathiafulvalene polymer (poly[K<sub>x</sub>(Ni-ttf)]) was found to have conductivities of over 100 S/cm.<sup>49</sup> The new material produced a powder that had increased electrical conductivity but significantly lowered the Seebeck coefficient.

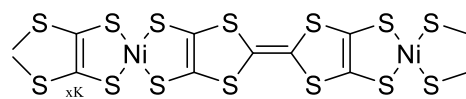
I also varied the reaction times. Sun *et al.*'s departure from previous literature included the lengthening of each reaction step to 12 hours.<sup>25</sup> A synthesis where each reaction step was allowed 4 hours was performed. However, a thick viscous gel was produced when the powder was mixed with the PVDF/DMSO solution and measurable films could not be made. Instead, a synthesis where no oxidation occurred was performed. However, no material was collected during the filtration step as the product did not have time to aggregate. The permeated solution was exposed to air for 5 minutes before it was filtered again. The second filtration collected enough material to be weighed. This resulted in improved performance and a subsequent synthesis with 30 minutes of air exposure was conducted. This synthesis gave significantly higher electrical conductivities leading to the optimization of the oxidation step. Temperature dependent thermoelectric property of this work is summarized in Fig. 5.

**Table 5:** Variation in synthesis procedure

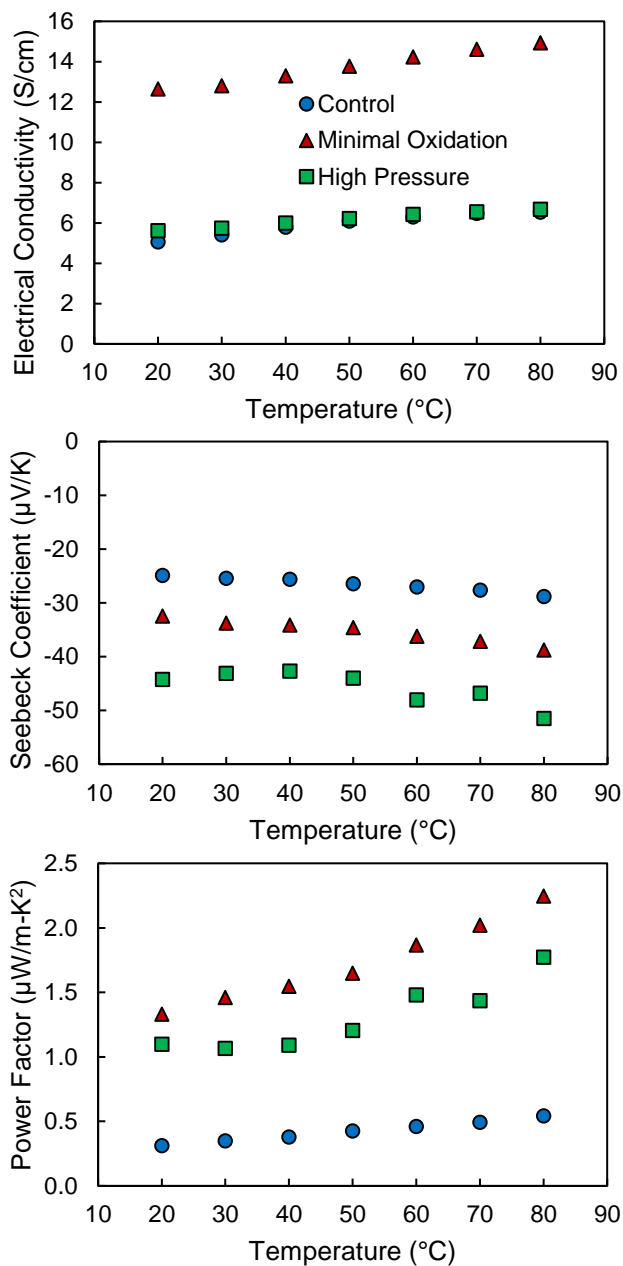
<b>Trial #</b>	<b><math>\sigma</math> (S/cm)</b>	<b><math>S</math> (<math>\mu</math>V/K)</b>	<b><math>S^2\sigma</math> (<math>\mu</math>W/m-K<sup>2</sup>)</b>
<b>Minimal Oxidation</b>	12.65 $\pm$ 0.12	-32.34 $\pm$ 0.86	1.32
<b>30 minute Oxidation</b>	56.53 $\pm$ 3.02	-28.62 $\pm$ 0.52	4.63
<b>Four Hour Reactions</b>	N/A	N/A	N/A
<b>High Pressure</b>	5.61 $\pm$ 0.21	-39.79 $\pm$ 0.28	0.89
<b>Copolymer</b>	15.78 $\pm$ .31	-5.43 $\pm$ .60	0.05



**Figure 4:** High pressure synthesis of ETT



**Scheme 2:** Structure of poly[ $K_x(\text{Ni-ett})$ ] and poly[ $K_x(\text{Ni-ttf})$ ] copolymer



**Figure 5:** Temperature dependent thermoelectric properties of poly[ $K_x(\text{Ni-ETT})$ ] with different reaction conditions.

Next, an optimization of the oxidation step was performed controlling the air-exposure time. Substantial amount of this work is described in more detail in Menon *et al.*<sup>61</sup> A single synthesis was performed where aliquots at different time intervals were taken and separated. While little changes are seen in Seebeck coefficient, electrical conductivity changes drastically with the highest conductivity found

in the ~40 minutes of air-exposure, as shown in Table 6. Result also show that the electrical conductivity quickly decays and begins to resemble the 24 hours' oxidation time.

**Table 6:** Variation of air exposure time during the poly[K<sub>x</sub>(Ni-ETT)] synthesis and the corresponding thermoelectric properties for ETT/PVDF/DMSO composite films at  $T = 300$  K.<sup>61</sup>

Exposure Time	$\sigma$ (S cm <sup>-1</sup> )	$S$ ( $\mu$ V K <sup>-1</sup> )	$PF$ ( $\mu$ W m <sup>-1</sup> K <sup>-2</sup> )
20	54 ± 4	-29 ± 2	4.5 ± 0.6
40	66 ± 7	-33 ± 3	7.2 ± 1.2
60	40 ± 4	-37 ± 4	5.5 ± 1.0
80	27 ± 1	-38 ± 3	3.9 ± 0.5

### ***Augmenting Poly[K<sub>x</sub>(Ni-ett)] Composite Properties Through Process Design***

Following synthesis optimization, alternatives in processing were also explored. Instead of a PVDF/DMSO solution, a PVDF solution in dimethyl formamide (DMF) was explored as shown in Table 7. All films found in Table 7 used material produced in Synthesis 3 found in Table 3. Films produced by the PVDF/DMF suspension typically have lower electrical conductivities and higher Seebeck coefficients, which disagrees with results found in Jiao *et al.*<sup>32</sup> Also Jiao *et al.*'s Supplementary Information with alternative solvents shows that PVDF/DMF solutions produce 2.95 S/cm films whereas PVDF/DMSO produce 2.26 S/cm films. However, it should be noted that the results found in Jiao *et al.*'s Supplementary Information contradicts the results in the main manuscript.<sup>32</sup> It was noted by Jiao *et al.* that while PVDF enables the poly[Ni<sub>x</sub>(Ni-ett)] to be solution processable, the insulating polymer matrix reduces the electrical conductivity of the material. Jiao *et al.* produced films of varying ETT to PVDF ratios from 1:1 up to 2:1.<sup>32</sup> In this work, we use a more dilute 10 mg PVDF/mL DMSO solution to prepare films in a 4:1

ETT to PVDF ratio. The resulting film produced slightly lower Seebeck coefficient but saw a 60% increase in electrical conductivity. The higher quality film and higher electrical conductivity is due to the removal of the insulating PVDF. This study showed that maximizing the ETT to polymer matrix ratio is yet another avenue for ETT film optimization. Another process change implemented is the use of spray coating; Spray coating offers another method of quickly producing thin films in large quantities. Despite DMSO having a high boiling point, uniform films were achievable through this method. Although lower performance was observed from spray-coating, this study shows the versatility of a ETT/PVDF suspension.

**Table 7:** Variations in fabrication techniques.

<b>Trial #</b>	<b><math>\sigma</math> (S/cm)</b>	<b><math>S</math> (<math>\mu\text{V/K}</math>)</b>	<b><math>S^2\sigma</math> (<math>\mu\text{W/m-K}^2</math>)</b>
<b>DMF Solution</b>	$1.51 \pm 0.06$	-34.49	0.18
<b>Dilute Solution</b>	$8.43 \pm 0.12$	-22.05	0.41
<b>Spray-Coat</b>	$2.11 \pm 0.28$	-26.18	0.14

To establish an optimal ETT to matrix ratio, the effect of different concentrations of PVDF/DMSO solutions was studied. This work is also described in Menon *et al.*<sup>61</sup> Higher mass ratios of ETT to PVDF exhibited higher electrical conductivities and lower Seebeck coefficients, as shown in Table 8. The temperature dependence of a 4:1 ETT:PVDF ratio is found in Figure 6. The higher conductivity is due to the exclusion of excessive PVDF in the insulating polymer matrix. While films can be produced with higher mass ratios, their film quality is poor. From this study, the results suggest that the insulating PVDF is a limiting factor. The next logical step is to substitute the PVDF with other film-forming polymers. Such candidates are PMMA and PVA, which have been explored by Jiao *et al.*, but also include n-channel polymers. Replacing PVDF with more conductive polymers presents an opportunity to further improve the thermoelectric properties. Table 9 lists properties of several composite films of ETT with various film-

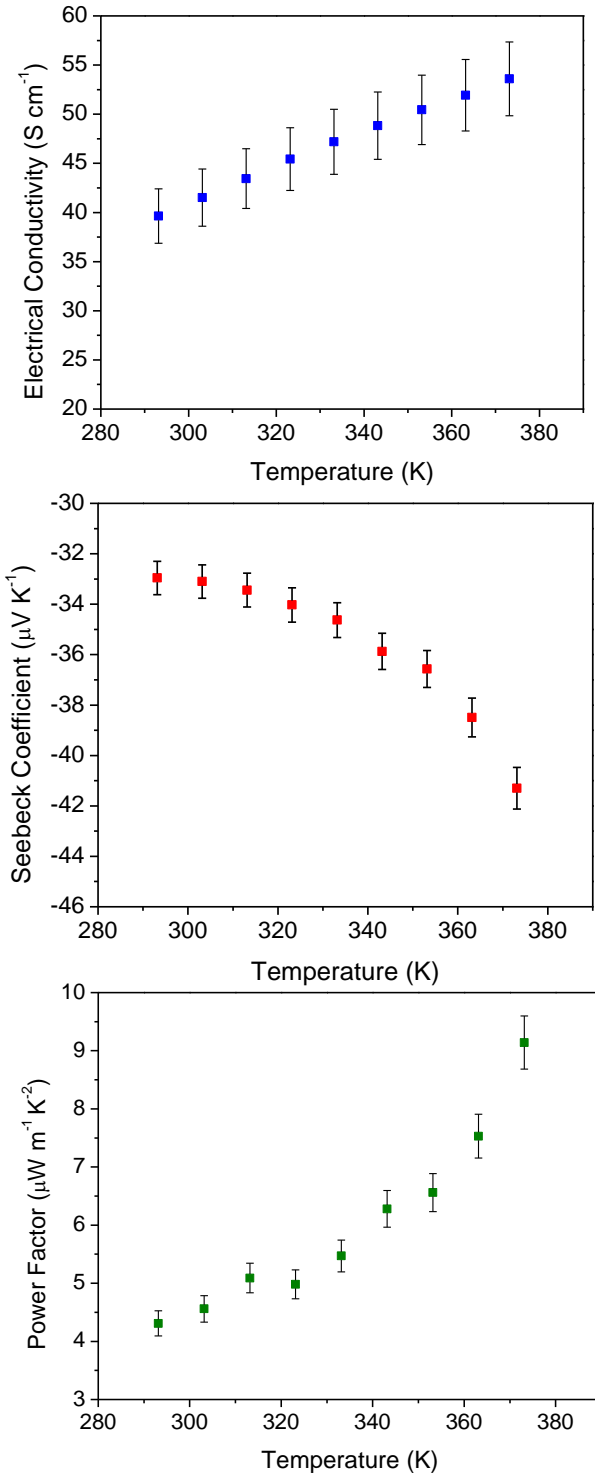
forming polymers. I tried to repeat Jiao *et al.*'s work with making films from PMMA and PVA with my highly conductive ETT.<sup>32</sup> The PMMA and PVA films that I produced differed significantly from Jiao *et al.*'s work; films produced exhibited electrical conductivity orders of magnitude lower and Seebeck coefficients twice as large in comparison.<sup>32</sup> However, it should be noted that I adapted the procedures for producing PVDF films and that Jiao *et al.*'s does not specify what ETT to polymer matrix ratios they used for their reported values.

Following making films from PMMA and PVA, we made films with n-channel polymers because it was speculated by Jiao *et al.*'s that PVDF's large and positive Seebeck coefficient plays a role in the composite's Seebeck coefficient.<sup>32</sup> I investigated substituting PVDF with known n-type polymers, therefore negative Seebeck coefficients, to optimize the composite's Seebeck coefficient. Furthermore, these polymers have the potential to be electrically conductive polymers with the addition of molecular dopants.<sup>62</sup> Substituting the PVDF with the n-channel polymers sharply increased Seebeck coefficients to almost quadrupled values found with PVDF. However, electrical conductivity also decreased significantly. ETT to polymer matrix ratio was increased to 8:1 ETT to polymer to determine if electrical conductivity can be improved as seen previously with PVDF. When the n-channel polymers were loaded with more ETT powder, electrical conductivity increased further while Seebeck decreased, as shown in Table 10.

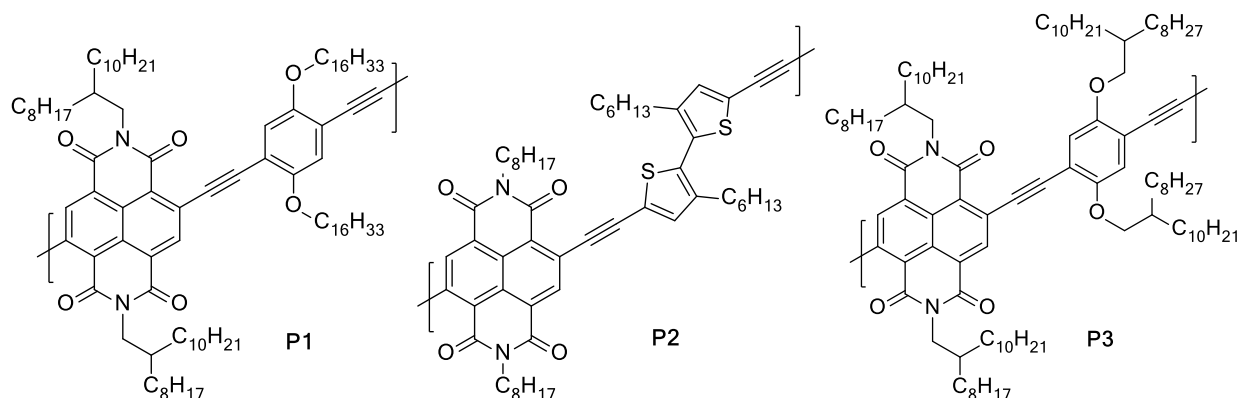
**Table 8:** Variation of thermoelectric properties ETT composite films with 30-minute air exposure at  $T = 300$  K for different ETT:PVDF mass ratios. 8:1 is not presented due to poor film quality resulting in unreliable property data.<sup>61</sup>

<b>ETT:PVDF/DMSO</b>	<b><math>\sigma</math> (S cm<sup>-1</sup>)</b>	<b><math>S</math> (<math>\mu</math>V K<sup>-1</sup>)</b>	<b><math>PF</math> (<math>\mu</math>W m<sup>-1</sup> K<sup>-2</sup>)</b>
2:1	$31 \pm 5$	$-36 \pm 2$	$4.0 \pm 0.7$
4:1	$42 \pm 4$	$-34 \pm 3$	$4.9 \pm 0.8$
6:1	$43 \pm 3$	$-33 \pm 4$	$4.7 \pm 0.9$
10:1	$62 \pm 6$	$-28 \pm 3$	$4.9 \pm 0.9$





**Figure 6:** Temperature dependent thermoelectric properties of poly[K<sub>x</sub>(Ni-ETT)] with 30 min air exposure: (a) Electrical conductivity and charge transport model, (b) Seebeck coefficient, and (c) power factor. Electrical conductivity of 4:1 ETT to polymer matrix mass ratio as a function of temperature. Reproduced from Ref. <sup>61</sup>



**Scheme 3:** Potential N-channel polymers used to substitute PVDF as a film-forming polymer. From left to right, polymers P1, P2, and P3 are respectively listed as Poly(4,9-((2,5-bis(hexadecyloxy)-4-(prop-1-yn-1-yl)phenyl)ethynyl)-2,7-bis(2-octyldodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone), Poly(4,9-((3,3'-dihexyl-5'-(prop-1-yn-1-yl)-[2,2'-bithiophen]-5-yl)ethynyl)-2,7-dioctylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone), and Poly(4,9-((2,5-bis((2-octyldodecyl)oxy)-4-(prop-1-yn-1-yl)phenyl)ethynyl)-2,7-bis(2-octyldodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone).

**Table 9:** Variations in the film forming polymer in a 4:1 ratio of ETT to polymer matrix by mass.

Sample ID #	$\sigma$ (S/cm)	$S$ ( $\mu\text{V/K}$ )	$PF$ ( $\mu\text{W/m-K}^2$ )
PVDF	56.5	-28.6	4.63
PMMA	< 0.001	-52.6	< 0.01
PVA	0.128	-54.9	0.04
P1	0.047	-74.9	0.026
P2	0.027	-116	0.036
P3	0.018	-113	0.023

**Table 10:** Additional ETT loading in an 8:1 ratio of ETT to polymer matrix by mass.

<b>Sample ID #</b>	<b><math>\sigma</math> (S/cm)</b>	<b><math>S</math> (<math>\mu\text{V/K}</math>)</b>	<b><math>PF</math> (<math>\mu\text{W/m-K}^2</math>)</b>
P1	3.00	-40.1	0.482
P2	1.03	-55.4	0.316
P3	2.05	-52.9	0.574

#### IV. CONCLUSION

In conclusion, the thermoelectric properties of poly[K<sub>x</sub>(Ni-ett)] can further be optimized without further complicating film processing. This work shows that poly[K<sub>x</sub>(Ni-ett)] produced from a reflux reaction can improve its power factor by over a factor of ten. The improvement was accomplished by first identifying the oxidation step as a method to improve electrical conductivity. Next, the oxidation step was optimized by determining the air exposure time for maximizing electrical conductivity. Finally, properties could be further augmented by reducing the concentration of the insulating PVDF matrix without compromising the integrity of the film. Other methods, such as changing reactant concentration and polymer matrix, were found to increase specific properties but resulted in an overall decrease in the thermoelectric performance of the material.

Moving forward, Poly[K<sub>x</sub>(Ni-ett)] has more opportunities to improve its thermoelectric properties. This work utilizes readily available air as an oxidation source and found that oxidation is key to increasing thermoelectric properties through synthesis. Chemical oxidation of poly[K<sub>x</sub>(Ni-ett)] has been explored previously with various oxidation agents, but these oxidation agents outside of air has never been used to investigate their effects on thermoelectric properties. Furthermore, doping is a common technique used to further improve thermoelectric properties of many other materials. However, poly[K<sub>x</sub>(Ni-ett)] has never been doped which makes doping with n-type dopants a potential pathway to further improve thermoelectric properties.

## APPENDIX A

**Table xx:** Synthesis of n-type ETT polymers. Data from references,<sup>25, 32, 44-45, 51, 53-54, 57-58, 63-64</sup>

Author	Reaction Environment	Solvent	Reaction Time After AOMe + TPD Addition	Reaction Time After NiCl <sub>2</sub> Addition	Oxidation Time (in air/O <sub>2</sub> )	Filtering Process and Solvents	Drying Time	Notes	$\sigma$ (S/cm)
Sun (2016) <sup>45</sup>	Inert	MeOH	36 hours	36 hours	N/A (see Notes)	1. H <sub>2</sub> O, 2. MeOH	24 hours	Potentiostatic deposition	67.5
Sun (2016) <sup>44</sup>	Inert	MeOH	36 hours	36 hours	N/A (see Notes)	N/A	24 hours	Potentiostatic deposition as a film then washed.	
Toshima (2015) <sup>57</sup>	Surfactant	MeOH	12 hours	12 hours	“awhile”	1. H <sub>2</sub> O, 2. MeOH, 3. Diethyl Ether	12 hours		<<1
Jiao (2014) <sup>32</sup>	Inert	MeOH	12 hours	12 hours	12 hours	1. H <sub>2</sub> O, 2. MeOH, 3. Diethyl Ether	12 hours	scaled-up by 7	8.31 - K
Massonnet (2014) <sup>64</sup>	Inert	MeOH	12 hours	12 hours	“awhile”	1. H <sub>2</sub> O, 2. MeOH, 3. Diethyl Ether	12 hours		N/A
Faulmann (2013) <sup>58</sup>	Addition of Ionic Liquid	MeOH	1.5 hours	3 hours				reactions at 100 °C; using surfactants; soluble product	<< 1
Sun (2012) <sup>25</sup>	Inert	MeOH	12 hours	12 hours	“awhile”	1. H <sub>2</sub> O, 2. MeOH, 3. Diethyl Ether	12 hours		40 – Na 44 - K
Yoshioka (1990) <sup>54</sup>	nitrogen (inert), possibly reduced pressure	MeOH	10 hours	1 hour	10 min	1. water, 2. MeOH, 3. Acetone, 4. Ether	vacuum	used Bu <sub>4</sub> N as final cation	2 - Na
Vogt (1988) <sup>53</sup>	Inert	MeOH	2-3 hours	2-3 hours	unknown	1. H <sub>2</sub> O, 2. MeOH, 3. Acetone	unknown		4 - Na
Vicente (1986) <sup>63</sup>	Inert	MeOH	2-3 hours	12 hours	unknown	1. H <sub>2</sub> O, 2. MeOH, 3. Acetone	unknown		3.8 - Na
Holdcroft (1985) <sup>51</sup>	Refluxed and degassed with nitrogen	EtOH	“few minutes”	Essentially zero	Various	1. Hot Water, 2. Acetone, 3. Hot Water	Overnight at 50 °C	"None" oxidation yielded highest conductivity	5.4 - Na

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