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Structure and conductivity studies of PTh-Ni composites

Chandraprabha G, T. Sankarappa*, Jyoti Kattimani, K. Praveenkumar, J.S. Ashwajeet and R. Ramanna
Department of Physics, Gulbarga University, Gulbarga-585106, Karnataka, INDIA

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Abstract

Polythiophene (PTh) has been made by chemical oxidation method at 275 K using FeCl3 as an oxidant. Nickel nanoparticles were synthesized by modified polyol process. PTh and Ni nanoparticles were mixed mechanically in different weight percentages and the composites were prepared. Pure PTh, Ni nanoparticles and composites were characterized by XRD and SEM techniques. Electrical conductivity of pure PTh and PTh-Ni nanocomposites has been investigated for the temperature range from 303 K to 473 K. Temperature variation of conductivity revealed semiconducting nature. Conductivity of the composites has been found to be decreasing with increase of Ni in the composites. Mott's Small Polaron Hopping (SPH) and Variable Range Hopping (VRH) models were applied to understand temperature behavior of conductivity. Activation energy for conduction and density of levels at Fermi energy were determined. Activation energy for conduction is found to be decreased with increasing weight percentage of Ni in the composites. For the first time PTh-Ni composites have been studied for temperature variation of conductivity and data analyzed thoroughly.

Keywords: Structure, conductivity, PTh-Ni, nanoparticles.

Introduction

Conducting polymers such as polyacetylene, polyaniline, polypyrrole, polythiophene, polyfuran etc. were studied for variety of applications like organic light emitting diodes, super capacitors and electron beam lithography etc[1-3]. Of these, Polythiophene (PTh) is an interesting and promising material due to its easy synthesis and environmental stability[4]. Also, the composites made of conducting polymers doped with inorganic materials like metals and metal oxide nano particles have drawn attention as they show properties of both the components. In conducting polymers, nanosized filler particles produce large interfacial area between the polymer and filler which enhance the properties of composites and which in turn increase their utility[5].

Polythiophene particles synthesized in the presence of a cetyl trimethyl ammonium bromide appeared spherical in shape and its conductivity was found to be $3.1X10^{-2}$ $\Omega^{-1}m^{-1}$ [6]. Polytiophenes synthesized in the presence of cations, anions and non-ions surfactants have shown amorphous nature and cyclic voltametry measurement revealed that Polythiophene prepared with non ionic surfactant found to be the suitable electrode materials for redox supercapacitors[7]. Spherical shape of polythiophene nanoparticles prepared by oxidative polymerization method has shown low surface resistivity and high thermal stability[8]. The conductivity of pure polythiophene synthesized by following oxidation method has been quoted to be $3.2X10^{-5}$ $\Omega^{-1}m^{-1}$ [9]. The room temperature conductivity of SWNT-PTh composite was $0.41X10^{2}$ $\Omega^{-1}m^{-1}$ while that of pure PTh measured $1.67X10^{-4}$ $\Omega^{-1}m^{-1}$ [10]. The electrical conductivity increased with increase of V_2O_5 content in PTh/V_2O_5 composites[11,12]. Conductivity of PTh/ZnO composite has been reported to be changing from 10^{-2} $\Omega^{-1}m^{-1}$ to 1 $\Omega^{-1}m^{-1}$ for the temperature range from 303 K to 473 K[13]. The electrical conductivity increased from $4.5X10^{-1}$ $\Omega^{-1}m^{-1}$ to 1.25 $\Omega^{-1}m^{-1}$ for PTh-Ni nanocomposites[14].

Keeping in view of the fact that there is no much work on conductivity of Polythiophene-Nickel nanocomposites, we synthesized Polythiophene(PTh)-Nickel(Ni) nanocomposites using separately prepared PTh and Ni particles. The samples were characterized by XRD, SEM and studied dc electrical conductivity as a function of temperature.

Material and Methods

HiMedia make AR grade Thiophene, Nickel(II) acetate tetrahydrate, and sd-fine make AR grade anhydrous $FeCl_3$, chloroform, methanol, 1,2 propandiol, Hydrazine hydrate 80%, Sodium hydroxide and Acetone were used to prepare Polythiophene and Nickel particles.

Polythiophene (PTh) preparation: Thiophene of 2ml was added to 70 ml of chloroform and kept for stirring for 15 minutes. 9 grams of $FeCl_3$ is added to 180 ml of chloroform and stirred for 15 minutes. $FeCl_3$ solution was added drop by drop to the thiophene solution and kept stirring for 24 hours by maintaining temperature of 275 K. The black precipitate of polythiophene formed was filtered and washed with chloroform. It was further washed with methanol and double distilled water several times to remove residual oxidant. The resulted brown powder has been dried in an oven[9].

Synthesis of nickel nanoparticles: Known quantities of nickel (II) acetate tetrahydrate in 50 ml of 1, 2 propandiol and sodium hydroxide in 50 ml of 1, 2 propandiol were dissolved separately at 333K. Both solutions were mixed together and stirred. To this solution, a reducing agent hydrazine hydrate of 80% concentration was added drop wise. The reduction process was allowed for 1 hr at temperature of 353K. Using magnet, black coloured nickel powder was separated from the solution, it was washed with methanol, double distilled water and acetone and dried in oven[15].

Synthesis of PTh-Ni composites: As prepared PTh and Ni nanoparticles were mixed in the weight percentages as $PTh_{100-x}Ni_x$. Where x = 10%, 20%, 30%, 40%, and 50% and named them as PTh-Ni1, PTh-Ni2, PTh-Ni3, PTh-Ni4 and PTh-Ni5 respectively.

X-ray diffraction studies were carried out in a X-ray powder diffractometer (model D2 PHASER). Surface morphology was observed at various magnifications in a Scanning Electron Microscope (model JSM 6360). The powder composites were pelletized using hydraulic press by applying a pressure of 20 kg/cm^2.

Temperature dependent electrical conductivity has been investigated for the temperature range from 303 K to 473 K by adopting two probe method. A constant voltage 5V was applied across the pellet, the current, I, passing through sample has been measured with the help of a picoammeter. Electrical Resistivity, ρ, has been estimated as $\rho = R (A/l)$, where $R = (V/I)$, A cross sectional area and l the thickness of the pellet. Conductivity, $\sigma = 1/\rho$ has been worked out.

Results and Discussion

XRD: XRD patterns of PTh, Ni nanoparticles and the composite PTh-Ni4 are shown in figures-1 (a-c).

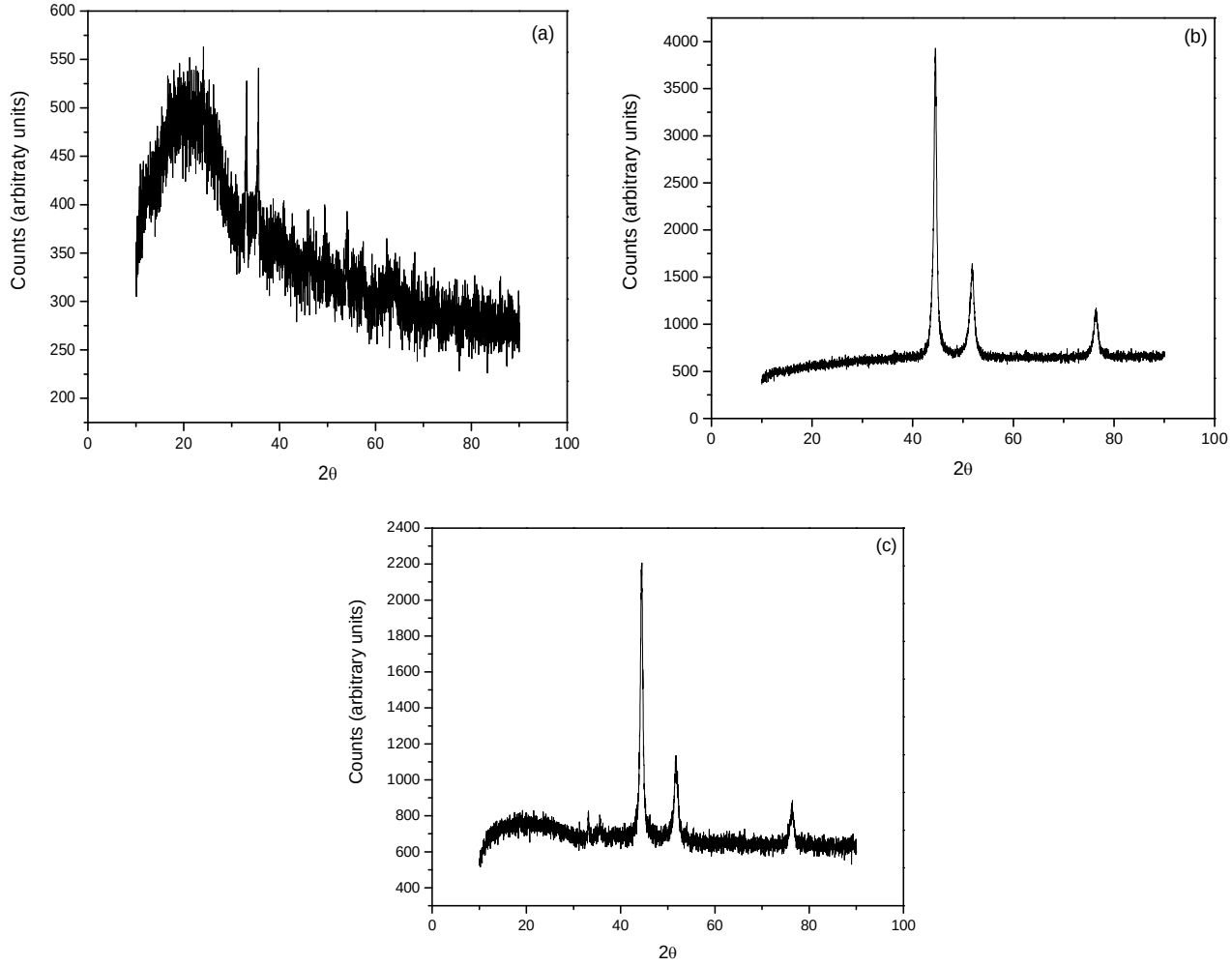


Figure-1
XRD patterns of (a) Pure PTh, (b) Ni nanoparticles and (c) PTh-Ni4

From the XRD pattern shown in figure-1(a), it can be seen that there is a broad peak centered and 2θ = 21.36˚ and two additional peaks at 2θ = 33.12˚ and 35.50˚. Broad peak advocates amorphous nature of PTh and two additional peaks may be due to any residual $FeCl_3$ particles left in the polymerization process. Similar conclusion was drawn in reference[6]. Additional peaks were observed in reference[16] and they were attributed to the development of crystallinity in PTh. Microwave synthesis of PTh also produced additional XRD peaks[17].

In figure-1(b), for nickel nanoparticles, the peaks observed at 2θ values of 44.50˚, 51.64˚ and 76.32˚ are in good agreement with the reported values in reference[15]. Grain sizes were calculated using Scherrer equation. Miller indices and interplanar spacing are also estimated and tabulated in Table 1. It is clear from the indexing that Nickel particles are in FCC structure and they are of nanosize.

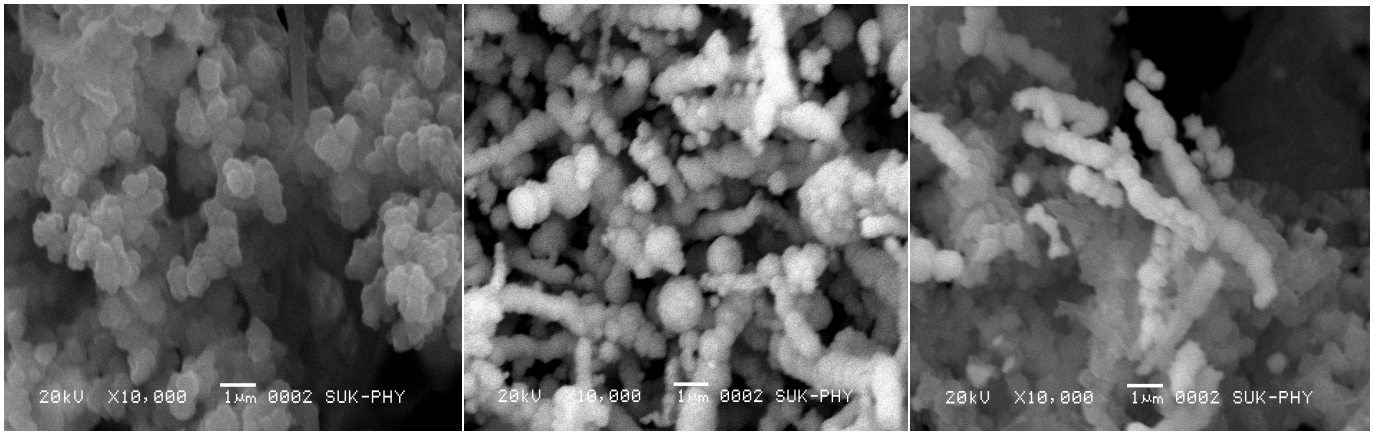
In XRD pattern of PTh-Ni4 composite, shown in figure-1(c), peaks observed are at 2θ values which are same as those observed for Ni particles. Additional peaks found in PTh pattern (figure-1(a)) are also seen in figure-1(c). This indicates that there is no structural change of any of the constituents occurring on their mechanical mixing. Similar XRD pattern has been observed for the remaining four composites.

From figure-2(a), morphology of PTh particles can be noted to be spherical. Figure- 2(b) reveals that Ni nanoparticles are also spherical in shape. Figure- 2(c) clearly shows the presence of Ni nanoparticles in the PTh host polymer.

Conductivity: The temperature dependent electrical conductivity of pure PTh and its composites have been measured in the temperature range from 303 K to 473 K. The conductivity values of pure PTh, and PTh-Ni nanocomposites at 303 K are tabulated in table-2. Conductivity of the composites decreased as the weight percentage of Ni is increased.

Table-1
Peak indexing, Interplanar distance and Grain sizes

Sample	2θ	Miller indices (hkl)	Interplanar distance d (Å)	Grain size (nm)
Ni nanoparticles	44.50˚	(111)	2.035	15.677
	51.64˚	(200)	1.765	4.623
	76.32˚	(220)	1.246	2.054



(a) **(b)** **(c)**

Figure-2
SEM images of (a) Pure PTh, (b) Ni nanoparticles and (c) PTh-Ni4

Table-2
Conductivity σ of pure PTh and PTh-Ni composites at 303 K

Samples→	PTh	PTh-Ni1	PTh-Ni2	PTh-Ni3	PTh-Ni4	PTh-Ni5
□□x 10^{-5} ($□^{-1}m^{-1}$)	8.003	3.797	3.312	2.513	2.108	1.719

A typical plot of conductivity, σ versus temperature, T is shown in figure-3(a) for pure PTh. It can be observed that conductivity increased with increase in temperature. This highlights the semiconducting nature of PTh. Conductivity variation with temperature is shown in figure-3(b) for the composite PTh-Ni4. It can be specifically noted that the composite PTh-Ni4 also exhibits semiconducting nature. Similar result has been obtained for the other four composites.

The temperature variation of electrical conductivity has been viewed in terms of Mott's Small Polaron Hopping (SPH) model. As per this model, conductivity is given by

$$\sigma = \frac{\sigma_o}{T}\exp(-\frac{E_a}{K_B T}) \quad (1)$$

Where σ_o is the pre exponential factor and E_a is the activation energy for small polaron hopping[18].

The plots of ln(σT) verses reciprocal temperature for all the samples are show in figure-4(a). Linear type of variation can be seen in the high temperature region. Therefore, linear lines were fit to the data and slope of which is used to calculate the activation energy (E_a). The variation of activation energy E_a and conductivity at 460 K, Pure PTh and all PTh-Ni nanocomposites are shown in figure-4(b).

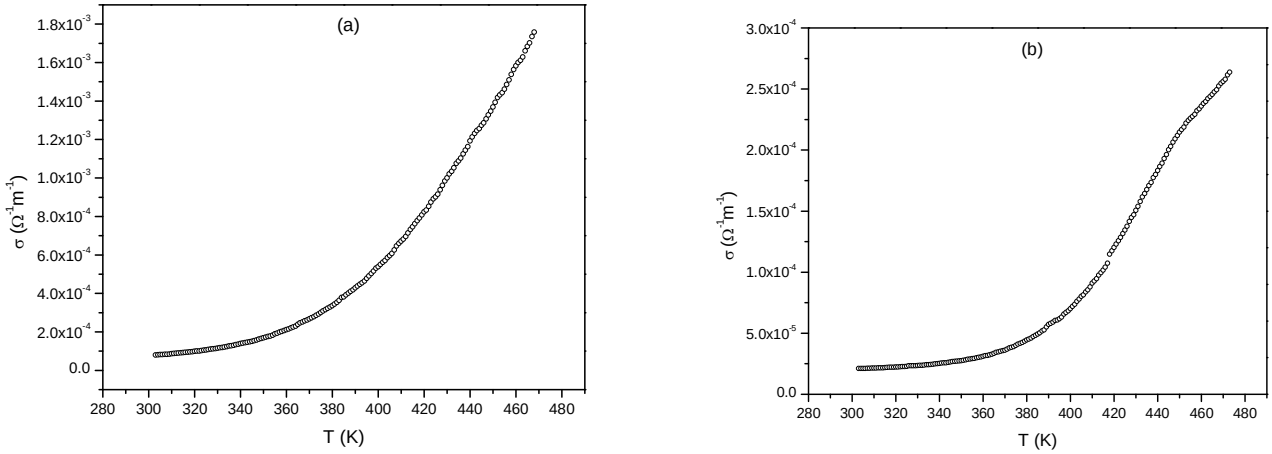


Figure-3
Conductivity σ variation with temperature for (a) pure PTh, (b) PTh-Ni4 respectively

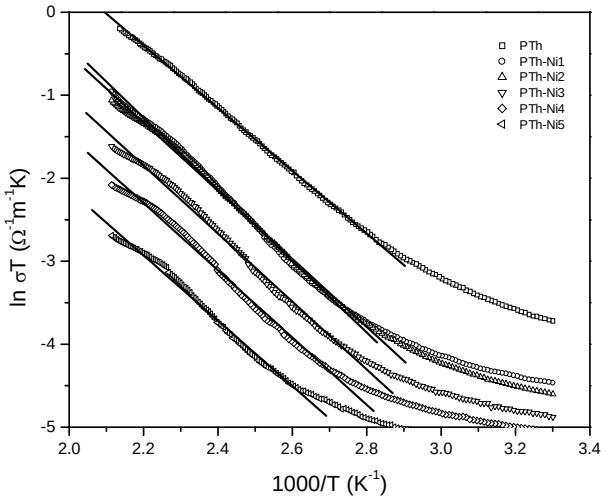


Figure-4(a)
Plots of ln (σT) versus (1/T) for pure PTh and PTh-Ni composites

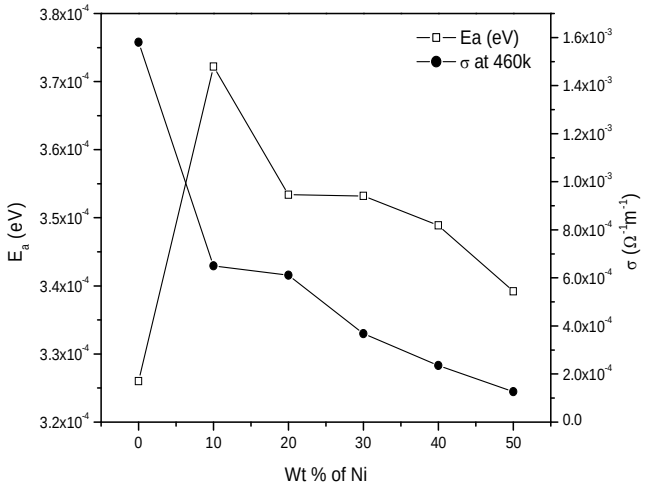


Figure-4(b)
Plots of activation energy, E_a and Conductivity, σ at 460 K versus wt % of Ni of PTh-Ni composites

It can be observed that conductivity of pure PTh is greater than composites. Further that both conductivity, σ and activation energy, E_a decreases with increase of weight percentage of Ni in the composites. This result points out that addition of Ni nanoparticles into PTh produces electrically insulating effect. Similar result has been reported for Fe nanoparticles doped PANI composites[19]. Decrease of E_a with increase of Ni nanoparticles content in the composites is somewhat puzzling and that needs to be understood. There are no reports found in the literature to this effect.

The data deviated from the small polaron hopping model has been fit to Mott's Variable range hopping (3D) model[11, 18, 20-22]. According to this model, conductivity is given by

$$\sigma = A\exp(-BT^{-\frac{1}{4}}) \quad (2)$$

$$A = 4\left[\frac{2a^3}{\pi k_B/N(E_F)}\right]^{\frac{1}{4}} \text{ and } \quad B = \left[\frac{e^3}{2(8\pi)^{\frac{1}{2}}}\right]V_O\left[\frac{N(E_F)}{\alpha K_B T}\right]^{\frac{1}{2}} \quad (3)$$

Where: Here N (E_F) refers to density of levels at Fermi energy, ν_o is the phonon frequency, wave fuction decay α^{-1} = 0.5 nm[23].

Plots of ln(σ versus ($T^{-1/4}$) for pure PTh and the composites are shown in Figure- 5. Linear fits were done to the data in the high temperature region and constants A and B were extracted. Using A and B, N(E_F) values were obtained and tabulated in Table. 3. These N(E_F) are in the range of 10^{28}-10^{30} $eV^{-1}m^{-3}$ and they are comparable to the values reported for Polythiophene-V_2O_5 and polypyrrole-Ag composites[11, 18].

Conclusion

Polythiophene has been prepared by chemical oxidation method and Nickel nanoparticles by modified polyol process. Composites of these two were prepared by mechanical mixing. As prepared materials were characterized using XRD and SEM. XRD of pure PTh revealed largely amorphous nature with two additional peaks which may be taken as signature for crystallinity of PTh itself or due to leftout $FeCl_3$ in the polymerization process. XRD patterns of composites indicated peaks corresponding to Ni and PTh. SEM images of the composites showed Ni nanoparticles well mixed up with PTh. Conductivity variation with temperature has been analysed using polaron-hopping models and activation energy for conduction and density of states were estimated.

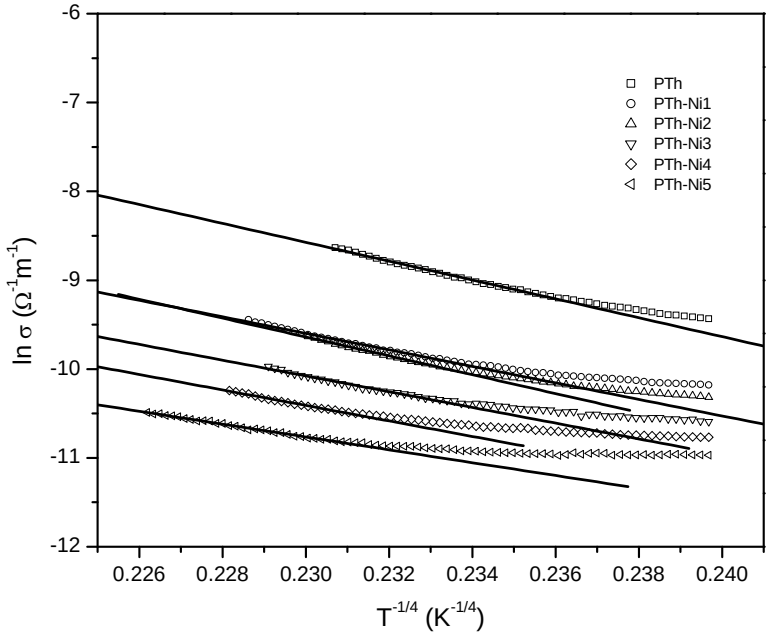


Figure-5
Plots of ln(σ versus ($T^{-1/4}$) for PTh and PTh-Ni composites

Table3
Density of states at Fermi level N (E_F) for all systems

Systems	PTh	PTh-Ni1	PTh-Ni2	PTh-Ni3	PTh-Ni4	PTh-Ni5
N(E_F) ($eV^{-1}m^{-3}$)	$2.661x10^{28}$	$8.705x10^{28}$	$3.525x10^{28}$	$1.488x10^{29}$	$1.942x10^{29}$	$1.422x10^{30}$

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