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Fabrication and Performance of Nd_{1.95}NiO_{4+δ} (NNO) Cathode supported Microtubular Solid Oxide Fuel Cells

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Abstract

Microtubular SOFC present significant advantages in comparison with the traditional planar SOFC configuration. In particular, the tubular design facilitates sealing and also reduces thermal gradients. As a consequence, rapid starts up times are possible. In addition, another advantage of the microtubular configuration is their higher power density per unit volume. Due to these properties, those devices are especially attractive for portable applications.

There has been a great interest in microtubular SOFCs in the recent years, mainly using anode supported cells. Electrolyte supported cells have also been reported, but there are relatively few investigations using the cathode as the support.

In the present paper, Nd_{1.95}NiO_{4+δ} (NNO) has been chosen as the cathode support, as it presents superior oxygen transport properties in comparison with other commonly used cathode materials, such as LSCF or LSM, and these material has been proven as an excellent cathode for SOFC and SOEC applications.

Results on the fabrication and characterization of NNO cathode supported SOFC will be presented. The tubes were fabricated by cold isostatic pressing (CIP) using NNO powders and corn starch as the pore former. The electrolyte (GDC based) was deposited by wet powder spray (WPS) on top of the pre-sintered tubes and then co-sintered. Finally, a NiO-GDC paste was dip-coated as the anode.

Optimization of the fabrication process as well as the electrochemical performance of single cells will be further discussed.

1. Introduction

Microtubular fuel cells have attracted a great interest in the recent years [1, 2]. In order to increase the variety of applications for Solid Oxide Fuel Cell (SOFC) applications such as auxiliary power units for automobile and power sources for portable devices, it is crucial to develop highly efficient small cell stacks which are robust for rapid temperature change operation. Until now, SOFC tubular designs were reported to be robust under thermal stress caused by a rapid heating cycle. By decreasing the tubular cell diameter is expected to improve the mechanical properties as well as volumetric power density of the cell stacks. In addition, another advantage of microtubular SOFCs is that they can accommodate repeated heat and electrical load cycling under rapid changes, as reported by different studies in the literature [3, 4].

First generation of microtubular SOFC were reported by Kendall and Palin [3] and Kilbride [5] using YSZ (yttria stabilized zirconia) electrolyte supports produced by extrusion techniques, and using nickel-zirconia cermet for the anode and lanthanum strontium manganite (LSM) as the cathode. As in planar configuration, current designs (second generation) are focused on electrode-supported cells. Anode supported is the preferred configuration as they have been widely studied by different research groups in the literature [6-11]. Cathode supported microtubular cells have been also investigated, although there is only a few works, in part due to the chemical reactivity between cathode and electrolyte during the co-sintering step of the fabrication process. For example, Liu et al. [12] reported cathode supported microtubular cells based on LSCF (lanthanum strontium cobalt ferrite)-GDC (gadolinia doped ceria) cathode supports. They achieved power densities of about 160 mW cm⁻² at 600 °C. Cathode supported cells based on LSM were also proposed by Zhao et al. [13] and reported power densities of 157 mW cm⁻² at 750 °C and 358 mW cm⁻² at 850 °C. Yamaguchi et al. [14, 15] also studied LSM cathode supported microtubular cells, using ScSZ (Scandia stabilized zirconia) as the electrolyte, an LSM-GDC activation layer between the support and the electrolyte and a NiO-GDC anode layer. Although they found signs of reactivity between GDC and ScSZ, they reported power densities as good as 453 mW cm⁻² at 750 °C.

Another interesting alternative for the SOFC cathode are the lanthanide nickelates (Ln = La, Nd, Pr), which have received considerable attention as materials for both solid oxide fuel cell (SOFC) electrodes and oxygen separation membranes [16-18]. These materials present a K₂NiF₄-type structure consisting of alternate LnNiO₃ perovskite layers and LnO rock-salt layers with excess oxygen atoms occupying the interstitial sites between the LnO layers. They also present flexible oxygen stoichiometry, leading to fast oxygen ion diffusion through bulk materials and rapid surface exchange kinetics. For implementation of these materials in devices, their phase stability is of great importance at temperatures up to 1000 °C and over a wide pO₂ range. Recently, Luebke reported for the first time the fabrication of microtubular SOFCs using neodymium nickelate (Nd_{1.95}NiO_{4+δ}, NNO) as the cathode support [19, 20].

In the present paper the fabrication and characterization of NNO cathode supported microtubular SOFCs using GDC as the electrolyte and NiO-GDC as the anode will be discussed.

2. Experimental

2.1. Cell fabrication

$\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ powders (Marion Technologies) were used for the fabrication of the supporting tubes. A Si-amount of about 1 at% is present as an endogenous impurity in the NNO powder. For the tube fabrication, NNO powders were mixed with corn-starch (pore former) and polyvinyl alcohol (PVA) as binder. Then, NNO tubes (figure 1) were fabricated by cold isostatic pressing (CIP) at 200 MPa and presintered at 900 °C. GDC-2%wt Cobalt-doped (Fuel Cell Materials) electrolyte was then deposited by wet powder spraying (WPS) using ethanol as liquid vehicle. NNO electrode-GDC electrolyte was co-sintered at 1300 °C for 2 hours. NiO-GDC (50%-50%wt) was used as the anode and was finally deposited by dip-coating and sintered at 1250 °C during 1.5 hours.

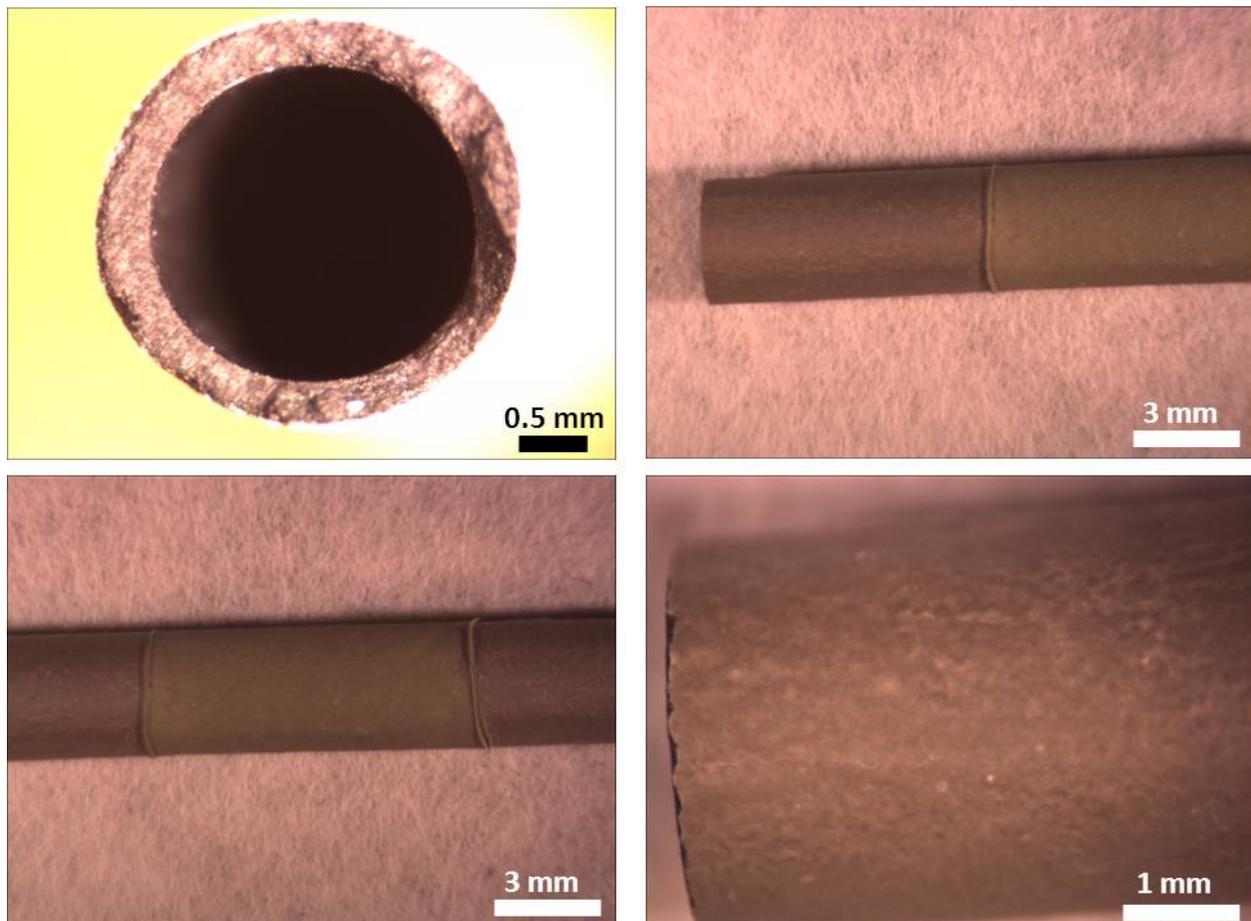


Figure 1: Details of the NNO cathode supported microtubular cell.

2.2. Experimental setup

Electrical connections were made using four platinum (Pt) wires. Pt mesh was used as current collector at the cathode side (inner of the tube) and nickel paste (terpineol based) was used as current collector at the anode. The tube was sealed using Ceramabond 503 sealant (Aremco, US) into alumina tubes and finally all the system was introduced into a quartz tube, and sealed again to separate both chambers. Additional details of the experimental setup can be found in ref. [21]. The cell was heated up to 600 °C in a small

tubular furnace under pure oxygen ($Q = 100$ ml/min) at the cathode side and static air at the anode side. At this temperature, Argon was introduced to purge the anode chamber during 10 minutes. After this, RT humidified hydrogen ($\sim 3\%$ H_2O) at 100 mls/min was introduced and the temperature was raised to 750 °C.

2.3. Electrochemical and microstructural characterization

Electrochemical measurements were carried out at temperatures between 600 °C and 750 °C. j -V and AC impedance measurements were recorded using a VSP Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, US). SEM images were obtained using a Merlin FE-SEM (Carl Zeiss, Germany).

3. Results and discussion

3.1. Microstructure of the cells

The microtubular cells are ~ 10 cm in length and the wall thickness of the NNO tube is ~ 350 - 400 μm , as observed in figure 1. The gas-tight GDC electrolyte and also the homogeneous distribution of the NiO-GDC anode layer can be also observed in figure 1.

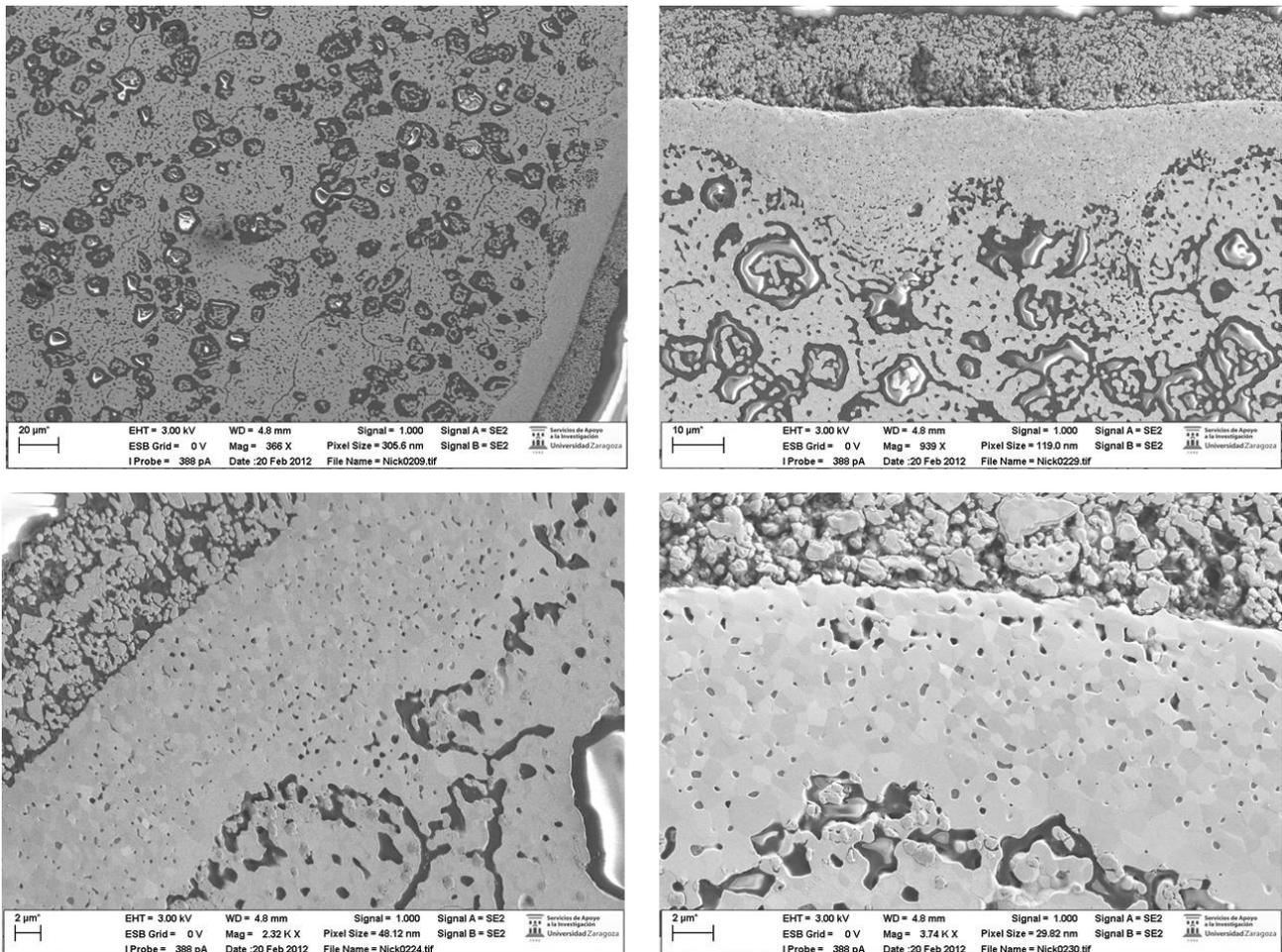


Figure 2: Microstructure of the NNO/GDC/Ni-GDC microtubular cell.

The microstructure of the cells can be observed in figure 2. A homogeneous distribution of porosity was achieved at the NNO support consisting of big pores of $\sim 10 \mu\text{m}$ (produced by the pore former) and submicrometric pores formed during NNO-GDC cosintering. A “root-tree like” interface can be also observed between the NNO and GDC phases assuring a strong interface between the cathode and the electrolyte. Thicknesses of both GDC electrolyte and Ni-GDC anode are about $15 \mu\text{m}$. It is also expected that at the sintering temperatures ($1300 \text{ }^\circ\text{C}$), Si will react with Nd to form neodymium silicate ($\text{Nd}_4\text{Si}_3\text{O}_{12}$) [19]. Ni precipitates at the interface as well as the formation of a mixed neodymium-cerium oxide ($\text{Nd}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8}$) were also predicted at the sintering temperatures [19]. EDX analysis confirmed the presence of Si (probably forming the neodymium silicate) and also nickel precipitates were observed at the NNO/GDC interface. We expect that this reactivity will not excessively affect the electrical properties and performance of the cells.

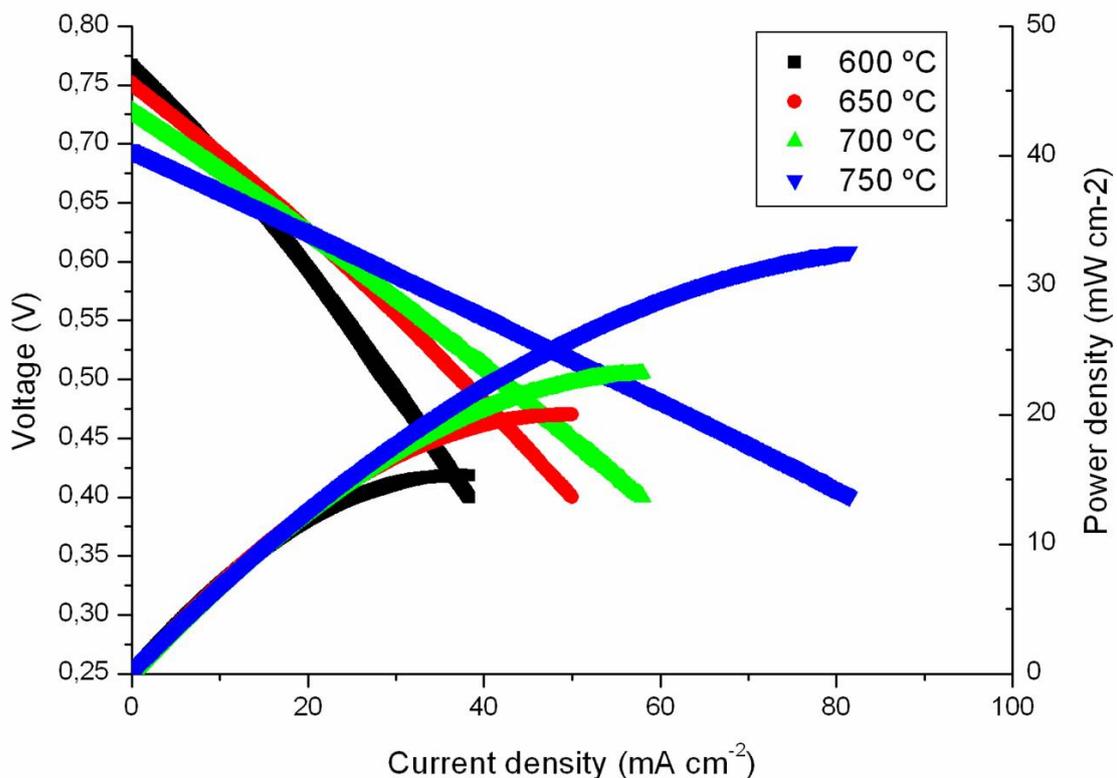


Figure 3: j-V measurements for the NNO/GDC/Ni-GDC microtubular cell.

3.2. Electrochemical characterization

OCV values for all the measured temperatures were lower than those predicted using the Nernst equation. As observed in figure 3, the measured values were 0.768 V, 0.753 V, 0.730 V and 0.696 V at 600 °C, 650 °C, 700 °C, and 750 °C, respectively. It is well known that the decrease in the OCV values can be attributed to an internal short circuit current related to the increase of electronic conductivity in ceria electrolyte due to reduction, as previously reported by other authors using thin layers of ceria electrolytes [22]. In order to solve this problem, we are currently developing cells with a second electrolyte layer, acting as an electronic blocking layer and as a consequence we expect to increase the OCV

values considerably. j - V curves are also shown in figure 3. Peak power densities of 16, 20, 24 and 33 mW cm^{-2} , at 600, 650, 700 and 750 $^{\circ}\text{C}$, respectively, were obtained. Although the performance is still modest in comparison with other cathode supported microtubular SOFC reported in the literature [12-15] we have demonstrated that nickelates are promising materials to be used as cathode supports for microtubular SOFC. All the subsequent studies will be focused on the microstructure development in order to increase fuel cell performance.

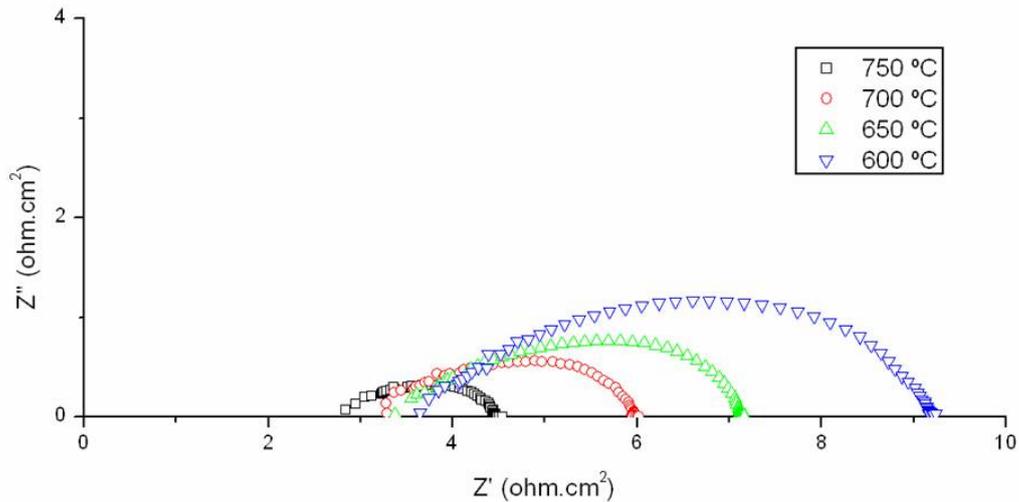


Figure 4: AC impedance collected prior to the j - V measurements for the NNO/GDC/Ni-GDC microtubular cell.

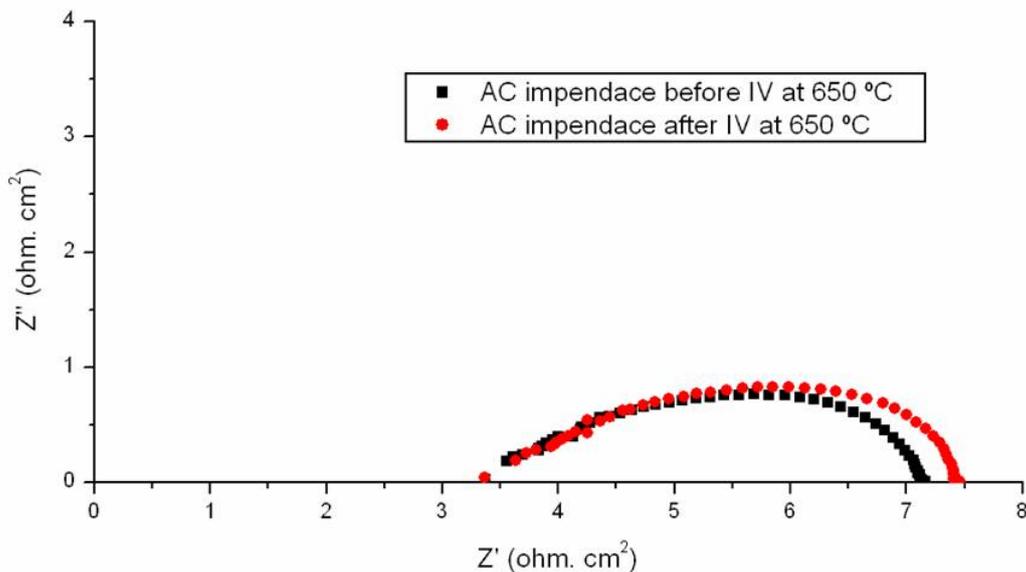


Figure 5: AC impedance collected before and after the j - V measurements at 650 $^{\circ}\text{C}$ for the NNO/GDC/Ni-GDC microtubular cell.

AC impedance results performed prior to each j -V curve as a function of the temperature are also shown in figure 4. It is remarkable that ohmic resistances are higher than those expected for a GDC electrolyte layer of about 15 μm , confirming that there is an extra ohmic polarization due in part to the reactivity at the NNO-GDC interface. Electrode polarization is also still large, especially at the lower temperatures (5.6 Ωcm^2 at 600 °C) and will need further improvement. At higher temperatures (750 °C) the polarization of both electrodes is reduced to 1.5 Ωcm^2 . Detailed studies by equivalent circuit fittings are currently under analysis in order to understand the reaction mechanisms to further improve cell components.

Finally, AC impedance experiments immediately before and after j -V measurement at 650 °C are presented in figure 5, showing a noticeable degradation taking place at the cell electrodes (total ASR was increased from 7.15 to 7.46 Ωcm^2). As a consequence, long term stability of the electrodes is also required to optimize the cells.

4. Conclusions

Results on the fabrication and characterization of neodymium nickelate cathode supported SOFC are presented. Peak power densities were 16, 20, 24 and 33 mW cm^{-2} , at 600, 650, 700 and 750 °C, respectively. Although the performance is still modest in comparison with other results reported in the literature we have demonstrated that nickelates are promising as cathode supports for microtubular SOFC. Further studies are required in order to avoid both electronic conduction of the GDC electrolyte to increase OCV values and chemical reactivity between the NNO support and the GDC electrolyte. Finally, optimization of the electrodes is also required.

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