Freeze tape casting is a means of making preforms of ceramic sheets that, upon subsequent completion of fabrication processing, can have anisotropic and/or functionally graded properties that notably include aligned and graded porosity. Freeze tape casting was developed to enable optimization of the microstructures of porous ceramic components for use as solid oxide electrodes in fuel cells: Through alignment and grading of pores, one can tailor surface areas and diffusion channels for flows of gas and liquid species involved in fuel-cell reactions. Freeze tape casting offers similar benefits for fabrication of optimally porous ceramics for use as catalysts, gas sensors, and filters.

Freeze tape casting includes, and goes beyond, traditional tape casting, in which an aqueous ceramic slip (ceramic and/or ceramic precursor particles suspended in water) is cast onto a poly(ethylene terephthalate) or poly(tetrafluoroethylene) carrier film by use of a doctor-blade assembly. The slip may also contain one or more organic solvent(s) plus a significant quantity of organic binders that make the tape strong and flexible after evaporation of the solvent(s). Traditional tape casting has been used to make ceramic sheets, for electronic and structural applications, ranging in thickness from 5 µm to 1,000 µm. Freeze tape casting expands this range to greater than 3 mm, thus eliminating the need for lamination steps in traditional processing.

An apparatus for freeze tape casting (see figure) is basically a traditional tape-casting apparatus augmented with a freezing bed. By use of the freezing bed, the water in the slip is frozen, from the bottom up through the thickness, immediately after the tape has been cast. For fabricating a porous ceramic, the freezing affords several advantages over traditional tape casting:

• In traditional tape casting, the water and any organic solvents are allowed to evaporate slowly before the tape is sintered to form the final ceramic. The evaporation can cause or be accompanied by undesired compositional and physical changes, including settling of particles out of suspension and density gradients. The freezing prevents such changes.
• Water alone or high melting point organic solvents (including benzene, cyclohexane, tertiary butyl alcohol, and camphene), can become formed into channels or other unique pore structures when directionally solidified. The channels or other pore structures can be tailored to some extent through control of the rate of freezing and/or the addition of such freezing additives as glycerol, glycols, antifreeze proteins, and/or alcohols.
• Porosity can also be tailored through choice of the concentration of suspended ceramic particles; typically, freeze-tape-cast ceramics contain open pore structures when the slips contain less than 45 volume percent of ceramic and/or metallic solids.
• In freeze tape casting, the solids loading can be made as low as 5 volume percent

In Freeze Tape Casting, a slip is cast into a tape as in traditional tape casting, but then, unlike traditional tape casting, the water and any other solvents in the tape are frozen. The frozen tape is then freeze-dried before sintering. (Temperature profile is indicated for an aqueous system)
to obtain exceptionally high porosity.

After casting and freeze-drying, the frozen tape is diced into sections for freeze-drying, in which the water and any other solvents are removed by sublimation. Because in sublimation, the solidified solvents are transformed into gases without passing through intermediate liquid phases, there are no capillary forces like those associated with liquid-to-vapor transitions that occur during drying in traditional tape casting. Because of the absence of capillary forces, the changes in the dimensions of microstructures in and the overall thickness of the tape are negligible and hence processing is simplified with the absence of cracks and other drying defects notable in traditional tapes. After freeze-drying, the sections of tape are cut into the desired shape, then sintered.

In the present method, instead of relying on the electrical conductivity of the substrate, one ensures that the substrate is porous enough that when it is immersed in an EPD bath, the solvent penetrates throughout the thickness, thereby forming quasi-conductive paths through the substrate. By making it unnecessary to use a conductive substrate, this method simplifies the overall EPD process and makes new applications possible. The method is expected to be especially beneficial in enabling deposition of layers of ceramic and/or metal for chemical and electrochemical devices, notably including solid oxide fuel cells.

In the initial application for which this method was invented, there is a requirement to fabricate unitary anode/solid electrolyte structures for solid oxide fuel cells, each such structure comprising the following:

- A porous cermet anode layer made of nickel and yttria-stabilized zirconia (YSZ) and
- A solid electrolyte in the form of a thin dense layer of YSZ.

The starting material for fabricating the structure is a porous layer consisting mostly of pellets of a composite of NiO and YSZ. The dense layer of YSZ is deposited on the NiO-YSZ composite later by means of EPD according to the present method, then the resulting (NiO-YSZ)/YSZ structure is sintered. The final fabrication step takes place after the sintered structure has been placed in a fuel cell: The reducing atmosphere maintained on the anode side of the fuel cell during testing reduces the NiO to metallic Ni, thereby creating the desired Ni anode having the porosity needed for transport of reactant and product gases.

The figure depicts the apparatus used in experiments to develop and demonstrate the present EPD method. The apparatus included a reservoir containing acetylacetone (as a nominally nonaqueous solvent). YSZ powder was stably suspended in the solvent by electrostatic repulsion, and YSZ particles were replenished to the depositing electrode by use of a magnetic stirrer. The YSZ particles acquired positive surface electric charges in a manner similar to that of surface charging in an aqueous medium. This charging has been conjectured to be a consequence of the presence of residual water in the acetylacetone. Regardless of the exact physical mechanism, the charging was fortuitous in that it contributed to the desired electrophoretic effect.

The NiO-YSZ deposition substrate was mounted on a stationary poly(tetrafluoroethylene) electrode holder and connected via a spring contact to the negative side of a DC power supply so that it became a deposition electrode (cathode). A platinum counter electrode was mounted on a movable poly(tetrafluoroethylene) electrode holder and connected to the positive side of the power supply, so that it became an anode. For most experimental