# FORMATION AND CHARACTERIZATION OF HIGHLY INTERFACIAL HYBRID NANOCOMPOSITES

**B.S. Mitchell**

*Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, USA*

**Abstract.** The formation and characterization of highly interfacial hybrid nanocomposites is described. The nanocomposites are formed by a two step, near net-shape manufacturing process that includes nanoparticle formation via high energy ball-milling followed by consolidation via hot isostatic pressing. Two types of hybrid materials are described: metal/ceramic nanocomposites, in which corrosion and mechanical properties are highlighted; and polymer/ceramic nanocomposites, in which proton conductivity is described. The influence of processing parameters and interfacial characteristics of the nanocomposites on selected properties are described, as well as recent advances in contamination control during nanoparticle formation and the effect of contaminants on nanocomposites properties.

## 1. INTRODUCTION

The high surface to volume ratios inherent to nanoparticles of all materials classes make them attractive for a variety of applications where surface area, interfacial area, and an ability to modify surfaces are important. Although most applications involve the formation and manipulation of surfaces, and some processes are strongly dependent upon surface properties; e.g., catalytic processes, there are some processes for which surface interactions have not been fully considered as playing an integral role. Such is the case for the effect of interfacial surfaces on bulk mechanical properties in nanocomposites. Considered here, through experimental examples, is the effect of interfacial surface area composition on the bulk properties of so-called 'highly interfacial' nanocomposite materials. First, the case of corrosion of aluminum/mullite nanocom-

posites will be considered, followed by a description of proton conduction in hybrid polymer/ceramic nanocomposite membranes.

## 2. EXPERIMENTAL

All nanocomposites were formed using near net-shape manufacturing technology (see Fig. 1), which involves high energy ball milling to form nanoparticles, followed by consolidation using Hot Isostatic Pressing (HIP). Aluminium/mullite nanocomposites were formed as previously described [1,2]. In brief, commercially available aluminum and mullite were milled in either stainless steel or nylon vials with the same grade milling media in a SPEX model 8000D (Metuchen, NJ) high-energy ball mill. The temperature was maintained at 0 °C by placing the unit in a temperature-controlled laboratory refrigerator. A

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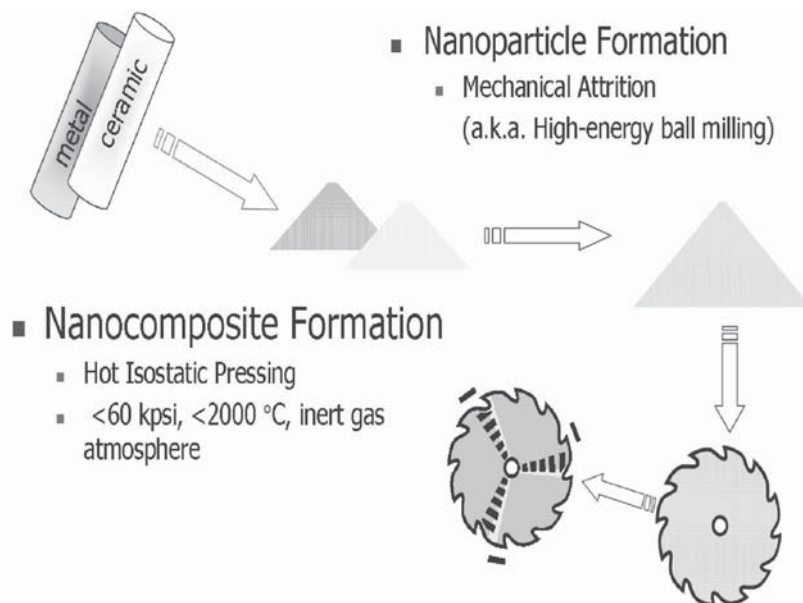Corresponding author: B.S. Mitchell, e-mail: brian@tulane.edu

**Fig. 1.** Schematic illustration of near-net shape manufacturing method.

description of the particle size distribution and grain size in the milled particles has been previously reported [2]. The powder samples were compacted in a stainless steel mold, then vacuum sealed. The preform was then placed into a Hot Isostatic Press (HIP) (AIP Inc, Columbus, OH). The HIPing was performed by applying isostatic pressure at 45,000 psi (nitrogen atmosphere) on the sample at 450 °C for 30 min. Corrosion studies were performed according to ASTM G 31-72.

Nafion-ceramic nanocomposites were formed in a similar manner, but with slight process modifications as previously described [3]. Nafion 1100EW, a perfluorosulfonated ionomer, was purchased in the form of pellets from Ion Power Inc. ($M_n$ = 13,000) and subjected to a sequence cryogenic milling at −196 °C in composite polycarbonate/stainless steel vials. PRONAS®, a proton-conducting crystalline oxide from Ceramatec, Inc. that belongs to the $Na_3Zr_2Si_4PO_{12}$ (NaSICON) family of materials, was ball milled in stainless steel vials. The nanoparticles were mixed, and pressed in a mechanical pressing at pressures of 7,000 - 8,000 psi and 165 °C to shape the membranes, then hot isostaticly pressed for 1 hour at 45,000psi and 35 −110 °C. Proton conductivity tests were performed on a Nafion 117 membrane hydrated and protonated in boiling 0.5M $H_2SO_4$, and an experimental 20% PRONAS/ 80% Nafion nanocomposite membrane without the pre-

hydration step. Both membranes were tested under identical conditions in wet hydrogen.

# 3. RESULTS AND DISCUSSION

**Aluminum/Mullite Nanocomposites.** The percentage aluminum loss in 0.1 M HCl for 24 hours ranged from about 20 to 25% in samples milled in stainless steel. However, in nylon milling media, the percentage aluminum loss was reduced to 3%. The type of milling media played a dominant role in nanocomposite corrosion resistance. Corrosion rates for samples containing aluminum only were 70.35 and 9.39 mpy when milled in stainless steel and nylonm respectively. Corrosion rates for the nano-composites containing 30% mullite were 40.5 and 6.3 mpy when milled in stainless steel and nylon, respectively. The corrosion observations can be explained in terms of grain boundary impurities. Impurities imparted during milling tend to move to the grain boundaries during the consolidation (HIPing) process. Heavy metals tend to be a starting point for corrosion [4]; this can be observed in the samples milled in stainless steel. Nylon undergoes thermal degradation during sample consolidation (HIPing) when the samples are exposed to 450 °C [1,2]. TEM analysis indicates that residual carbon from nylon decomposition forms on the surface of the aluminum grains (Fig. 2), and segregates to the grain boundaries. Samples milled in stainless steel show intergranular corrosion which occurs if the area around
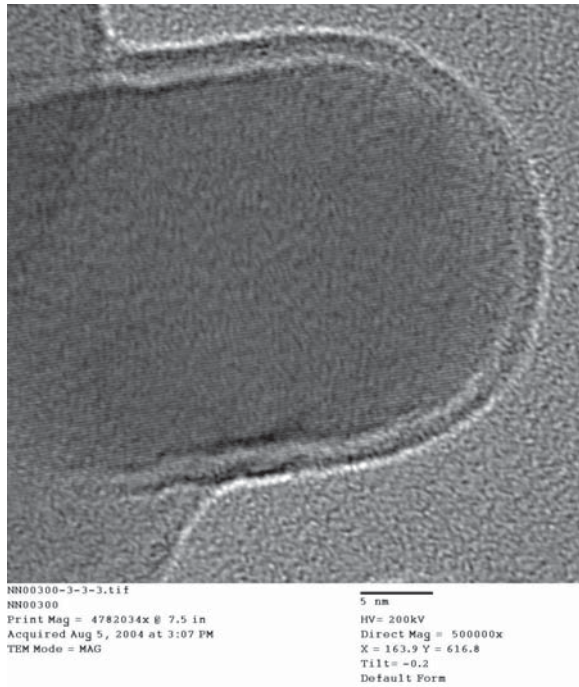
**Fig. 2.** Transmission electron micrograph of aluminum nanoparticle milled in nylon media.

**Table 1.** Conductivity of commercial and experimental nafion/pronas nanocomposite membranes.

| Membrane | Conductivity (S/cm) | | Relative |
|---|---|---|---|
| | 67 °C | 42 °C | Humidity |
| Nafion 117 | $1.0 \cdot 10^{-2}$ | $7.9 \cdot 10^{-3}$ | 99 % |
| Composite | $6.6 \cdot 10^{-2}$ | $4.3 \cdot 10^{-2}$ | 99 % |

[3]. The results of hydrogen conductivity tests on commercial Nafion and experimental Nafion/PRONAS membranes are shown in Table 1. The near net-shape manufactured membranes show a six-fold increase in proton conductivity over commercially-available membranes. In addition to enhanced proton conductivity, these membranes have the potential for improved thermal stability and high-temperature mechanical properties, as evidenced by an increase in the glass transition temperature, $T_g$, which results from the HIP operations (see Fig. 3).

the grain boundaries is less resistant than the matrix. Here, impurities such as iron, copper, nickel segregate at the grain boundaries during sample consolidation. These regions are depleted of these elements when exposed to a corrosive environment. After the initial depletion of the impurities, the acid then attacks the matrix causing cracks.

**Nafion/PRONAS Nanocomposites.** The formation and characterization of Nafion nanoparticles by mechanical attrition has been previously described

## 4. CONCLUSIONS

The enhancement of properties in metal/ceramic and polymer/ceramic nanocomposites formed by near net-shape processing is described. Corrosion properties in aluminum/mullite nanocomposites are improved due to carbonaceous species in the nanoparticle interfacial regions imparted during milling and HIPing. Similarly, hydrogen conductivity in Nafion/PRONAS Nanocomposites are improved due to favorable polymer-ceramic nanoparticle interactions.
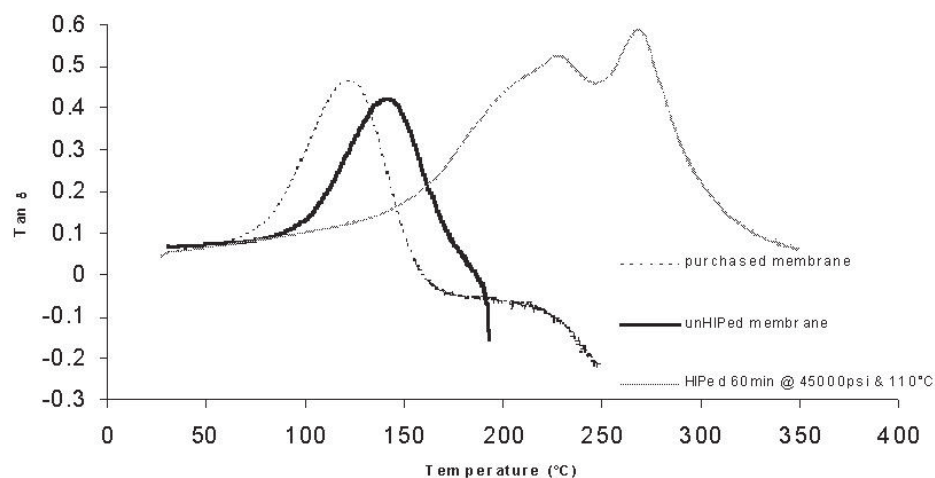


**Fig. 3.** Dynamic mechanical analysis of commercial and experimental (HIPed and unHIPed) nafion membranes.

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