

Developments in the use of Functionalized Boron Nitride in Composite Membranes for PEM Fuel Cells Applications

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Boron nitride (BN) has a structural formation based on boron and nitrogen atoms in the direction of the lattice. These structures are amorphous, hexagonal, cubic, and radical in shape. Hexagonal boron nitride is an excellent proton conductor at room temperature with a monolayer h-BN; at higher temperatures [1]. A reasonable proton conductor should be an ideal polymer electrolyte membrane with electrical insulator properties. H-BN is only in its early stages as a composite membrane filler used in fuel cells. There have been very few efforts to evaluate the use of h-BN in polymers composite. Chemical Functionalization of Boron Nitride: BN is functionalized to enhance the surface reactivity and the acidity. Functionalizing of BN is very hard as only less 5% of amino groups are present on the surface. There are many approaches to functionalize boron nitride before it is added to the material: A) Hydroxyle group: According to literatures, introducing hydroxyle group is the most common way to chemically functionalize boron nitride. Various method are available to functionalize BN with hydroxyle with acidic or base treatment. The method that seems most effective is acidic treatment followed by oxidizing agent such as H₂O₂ and KMnO₄ [1]. B) Sulfuonic groups: Sulfonation of BN is great option when the ionic conductivity is important. The free B bond is not strong enough to keep sulfonic group, thus, a medium is needed to attach SO₃ to BN. However, MTPS can be used for the sulfonation process by adding it mixed with toluene at 80°C [2]. C) Halogens: In an attempt to maximize the performance of BN, fluorination of BN was done. By heating the mixt of graphene sheets and XeF₂ fluorination of a suspended graphene monolayer can be occur, in which each carbon atom is covalently attached with a fluorine atom. The same process were done on BN to fluorinate it. The synthesized F-BN showed excellent physiochemical and electrical properties [3]. D) Others: Apart from the abovementioned methods, other groups and elements such as ammonia have been introduced to functionalize BN.

There are several polymer electrolyte membranes were modified with boron nitride to overcome the limitation related to polymers properties and to enhance the protonic conductivity, number of these composite membrane are: Proton conducting composite membranes are prepared by mixing Nafion and nano hexagonal boron nitride (NhBN) particles. At dry conditions, the maximum proton conductivity was measured as 0.005 S/cm at 150C for NafBN10, which is much higher than the pure Nafion [4]. Polybenzimidazole/boron nitride (PBI/BN) based composite membranes have been prepared for high-temperature PEM fuel cell. In addition to the excellent stability, the best conductivity was found 0.260 S/cm for PBI/BN-2.5 membrane at 180°C[5]. Reinforced HBN porous sulfonated poly(ether

sulfone) (PSPES) nanocomposite membranes with excellent proton conductivity and stability via modified non-solvent-induced phase inversion were prepared, in which shows an excellent proton conductivity of 77.4 ± 3.87 mS cm⁻¹ at 80 °C with 100% humidity[6]. Sulfonated poly-ether-ether-ketone (SPEEK)-hexagonal boron nitride (h-BN) (SPEEK-h-BN) nanocomposite membranes: It is observed that the SPEEK-5% h-BN membrane performs better than pure SPEEK membrane, has storage capacity of 2.98 wt. % at 150 oC and the adsorbed hydrogen has an average binding energy of 0.38 eV with high enhancement in teh thermal stability [7]. Other few exfoliated BN sheets and nanotubes have been studied for fuel cells applications. For instance, the addition of 3 wt% AH-BN into SPEEK-PES enhance the conductivity of 79.8 mS cm⁻¹ and power density of 131.1 mW cm⁻² at 80 °C[1]. The development of BN compsoite membranes in PEM fuel cells applications is still ongoing as it overcomes plenty of the membrane limitations especially the nonperflurinated ones.

References:

- [1] Yadav, Vikrant; Kulshrestha, Vaibhav (2019). Boron Nitride a Promising Material for Proton Exchange Membranes for Energy Applications. *Nanoscale*, 11, 12755-12773.
- [2] Abhishek Rajput;Savan K. Raj;Jeet Sharma;Nehal H. Rathod;P.D. Maru;Vaibhav Kulshrestha; (2021). Sulfonated poly ether ether ketone (SPEEK) based composite cation exchange membranes for salt removal from brackish water . *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 614, 126157.
- [3] Zhang, Zhuhua; Zeng, Xiao Cheng; Guo, Wanlin (2011). Fluorinating Hexagonal Boron Nitride into Diamond-Like Nanofilms with Tunable Band Gap and Ferromagnetism. *Journal of the American Chemical Society*, 133(37), 14831–14838.
- [4] Akel, Mert; Ünügür Çelik, Sevim; Bozkurt, Ayhan; Ata, Ali (2014). Nano hexagonal boron nitride-Nafion composite membranes for proton exchange membrane fuel cells. *Polymer Composites*, 37(2), 422-428.
- [5] Dedar Emad Hussin, Yağmur Budak, Yılser Devrim (2021). Development and performance analysis of polybenzimidazole/boron nitride composite membranes for high-temperature PEM fuel cells. *Energy research*,46 (4), 4174-4186.
- [6] Gayathri Ravi Kumar, Raja Pugalenth M, Guozhong Cao, and Ramesh Prabhu Manimuthu 2022, Reinforced Hydroxylated Boron Nitride on Porous Sulfonated Poly(ether sulfone) with Excellent Electrolyte Properties for H₂/O₂ Fuel Cells *Energy & Fuels* 2022 36 (12), 6445-6458.
- [7] Yadav, Vikrant; Rajput, Abhishek; Rathod, Nehal H.; Kulshrestha, Vaibhav (2019). Enhancement in proton conductivity and methanol cross-over resistance by sulfonated boron nitride composite sulfonated poly (ether ether ketone) proton exchange membrane. *International Journal of Hydrogen Energy*, 45(34), 17017-17028



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