

## Innovative Grafting of Polyvinylpyrrolidone onto Polybenzimidazole Proton Exchange Membranes for Enhanced High-Temperature Fuel Cell Performance

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**Abstract :** As a promising sustainable alternative to traditional fossil fuels, fuel cell technology is highly favoured due to its enhanced working efficiency and reduced emissions. In the context of high-temperature fuel cells (operating above 100 °C), the most commonly used proton exchange membrane (PEM) is the Polybenzimidazole (PBI) doped phosphoric acid (PA) membrane. Grafting is a promising strategy to advance PA-doped PBI PEM technology. The existing grafting modification on PBI PEMs mainly focuses on grafting phosphate-containing or alkaline groups onto the PBI molecular chains. However, quaternary ammonium-based grafting approaches face a common challenge. To initiate the N-alkylation reaction, deacidifying agents such as NaH, NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, etc., can lead to ionic crosslinking between the quaternary ammonium group and PBI. Polyvinylpyrrolidone (PVP) is another widely used polymer, the N-heterocycle groups within PVP endow it with a significant ability to absorb PA. Recently, PVP has attracted substantial attention in the field of fuel cells due to its reduced environmental impact and impressive fuel cell performance. However, due to the poor compatibility of PVP in PBI, few research apply PVP in PA-doped PBI PEMs. This work introduces an innovative strategy to graft PVP onto PBI to form a network-like polymer. Due to the absence of quaternary ammonium groups, PVP does not pose issues related to crosslinking with PBI. Moreover, the nitrogen-containing functional groups on PVP provide PBI with a robust phosphoric acid retention ability. The nuclear magnetic resonance (NMR) hydrogen spectrum analysis results indicate the successful completion of the grafting reaction where N-alkylation reactions happen on both sides of the grafting agent 1,4-bis(chloromethyl)benzene. On one side, the reaction takes place with the hydrogen atoms on the imidazole groups of PBI, while on the other side, it reacts with the terminal amino group of PVP. The XPS results provide additional evidence from the perspective of the element. On synthesized PBI-g-PVP surfaces, there is an absence of chlorine (chlorine in grafting agent 1,4-bis(chloromethyl)benzene is substituted) element but a presence of sulfur element (sulfur element in terminal amino PVP appears in PBI), which demonstrates the occurrence of the grafting reaction and PVP is successfully grafted onto PBI. Prepare these modified membranes into MEA. It was found that during the fuel cell operation, all the grafted membranes showed substantial improvement in maximum current density and peak power density compared to unmodified one. For PBI-g-PVP 30, with a grafting degree of 22.4%, the peak power density reaches 1312 mW cm<sup>-2</sup>, marking a 59.6% enhancement compared to the pristine PBI membrane. The improvement is caused by the improved PA binding ability of the membrane after grafting. The AST test result shows that the grafting membranes have better long-term durability and performance than unmodified membranes attributed to the presence of added PA binding sites, which can effectively prevent the PA leaching caused by proton migration. In conclusion, the test results indicate that grafting PVP onto PBI is a promising strategy which can effectively improve the fuel cell performance.

**Keywords :** fuel cell, grafting modification, PA doping ability, PVP

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