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Electrochemical Properties of Imidazole Tetrafluoroborate Ionic Liquid Grafted SPEEK Proton Exchange Membrane Doped by La_2O_3

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The membranes of sulfonated poly(etheretherketone) with 63.05% sulfonation degree were grafted by imidazole tetrafluoroborate ionic liquid (BF) firstly, and then doped by La_2O_3. It is concluded that BF can significantly improve the proton conductivity and methanol concentration of the composite membranes while grafting more BF on its backbone. Comparing ordinary physical doping, chemical graft could effectively avoid the loss of ionic liquid and extend the using life of membranes. Moreover, these serial samples also had a good effect on thermal stability compared with pure SPEEK. After continuously doped by La_2O_3 nanoparticles, it seems that more amount of La_2O_3, better methanol resistance reached. However, La_2O_3 had nothing to do with enhancement of proton conductivity even lower it. When doped by La_2O_3, coordination reaction occurs at the electron-donating groups which are riched on SPEEK backbone and generated mutual attraction between sulfonic acid groups, reducing the number of sulfonic acid groups and blocking the methanol diffusion path. This could ultimately lead to reducing methanol permeation concentration of the modified membranes. Specimen B0505 had overall excellent properties mentioned above.

Keywords: graft**,** imidazole tetrafluoroborate ionic liquid, SPEEK, properties

1. INTRODUCTION

Sulfonated poly(etheretherketone) (SPEEK) membranes have been paid more attentions to its good properties comparing to Nafion membrane [1-3]. But, it is also has some insufficient should be enhanced at high temperature and low humidity. In the last decade, physical doping modification (SiO_2,

Y_2O_3, W_2O_3, PES, PPSU, etc. [4-8]) and chemical grafting modification (PWA, ionic liquids, chemical crosslinking, etc. [9-13]) had been researched according to the improving its performance.

In the previous studies, it is found that Ionic liquid could slightly increased the proton conductivity by physical doping but does not meet the requirements of PEM methanol permeability and anti-swelling properties [14]. However, the doped particles or macromolecule are easier to outflow to reduce the performance and the service life due to physical blend. Its overall performance is less than pure SPEEK membrane. The performances of SPEEK proton exchange membrane increased, but the proton conductivity has not reached of 10^{-2} S•cm^{-1}. Thereby, choosing grafted SPEEK to improve overall application performance. 64.5% sulfonation degree of the SPEEK resin was selected in order to ensure the behaviors of methanol permeability and water swelling, and then grafted ionic liquid groups by a chemical substitution reaction to SPEEK to be formed novel polymer as SPEEK backbone with ionic liquid large molecule pendant. This technique differs from the doping modified. Through chemical grafting can solve the stability and working life of the membrane, and also can control the number of sulfonated functional groups on the side groups, greatly improve the proton conductivity. All over cannot be achieved by any other doping, blending technologies.

Rare earth oxide can be employed to maintenance of fuel cell anode (cathode). Wu [15] put Y_2O_3 into SPEEK system. Consequently, because of the neutral reactions happened between Y_2O_3 and sulfonic groups, proton conductivity was doomed to decreasing while methanol resistance enhanced excellently. Wang [16] blended both different molar ionic liquids and Y_2O_3 into SPEEK. As a result, both proton conductivity and methanol resistance of SPEEK/EB/Y_2O_3 were superior to pure one, but it seemed physical blend wasn't as steady as chemical one for long time used especially in high temperature and always destroyed polymer structural regularity.

In this paper, based on intermediate sulfonation SPEEK (63.05%), imidazole tetrafluoroborate ionic liquid (BF) was synthesized and grafted it to SPEEK backbones. Then doped the grafted SPEEK with certain amount La_2O_3 to prepare membranes to investigate the proton conductivity, methanol resistance and water uptake properties.

2. EXPERIMENTAL SECTION

2.1 The preparation of grafted SPEEK membranes

Poly(etheretherketone) was obtained from Chemistry Department of Jilin University (Jilin, China), in the form of particle. The same procedure was described in reference [17], and SPEEK had degree of sulfonation 63.05% (DS). $NaBH_4$ was utilized to carbonyl reduction of SPEEK (named as R-SPEEK) (figure 1, 2-3). Thirdly N-methylimidazole, offered by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), was at same molar ratio mixed with ammonium fluoroborate from Ao Xin Chemical Co., Ltd at room temperature for 12 h to synthesize imidazole chloride ionic liquids CL (figure 1, 2-1). Equimolar quantities CL and $NaBH_4$ were sent to 50 mL dichloromethane to react 24 h at 40 °C to synthesize [Smin]BF_4 (figure 1, 2-2). Then certain amount BF was grafted into SPEEK backbone by reacting with R-SPEEK solution (figure 1, 2-4). Finally, different molar mass La_2O_3, from Shanghai Huaming Gaona Rare Earth New Materials Co., Ltd with a particle size of 100 nm, was adopted into the grafted solution with mechanical stirring. Grafted SPEEK composite membranes were obtained by casting their viscous solution onto a glass plate. The thickness of the dried composite membranes was about 100 μm. Contents of membranes were described in Table 1.

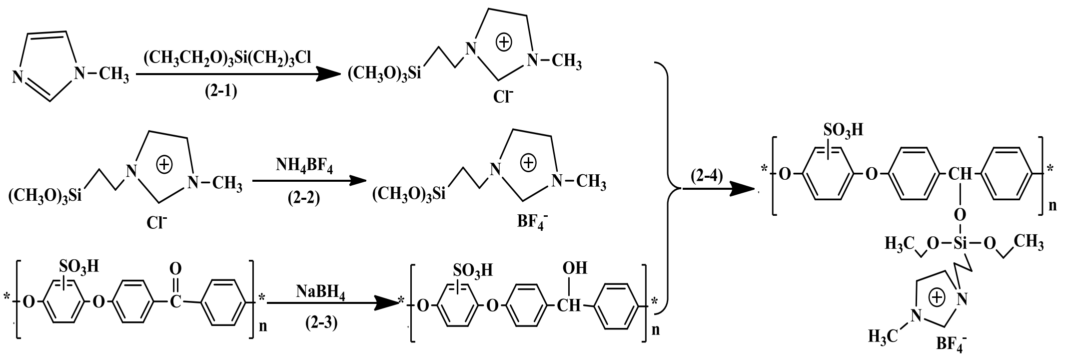

Figure 1. Synthesis of grafted SPEEK

Table 1. Contents of composite membranes specimens

CODE	SPEEK (wt.%)	Ionic liquids (wt.%)	La_2O_3 (wt.%)
SPEEK	100	0	0
B0500	95	5	0
B1000	90	10	0
B0501	85	15	0
B0505	80	15	5
B0510	75	15	10

2.2 The characterization and testing

Fourier transform infrared (FTIR) spectra of the reactants were recorded with AVATAR 370 infrared spectrometer (Thermo Nicolet Instrument Co., USA) in the scanning range of 600-4000 cm^{-1}. All specimens were liquid which characterized by painting on the surface of glass slide directly.

Proton conductivity of membrane specimens in the traverse direction were measured in a measurement cell using AC Electrochemical Impedance Spectroscopy, which consists of a Solartron Instruments 1287 electrochemical interface and a Solartron Instruments 1255 B frequency response analyzer (UK) [18]. The EIS recorded over a frequency range of 1-10^6 Hz. Before the tests, all membrane specimens were abundantly immersed in 1 mol/L hydrochloric acid solution for 24 h then rinsed with de-ionized water several times. Consequently, resistance of membranes was measured and proton conductivity was calculated as described.

Methanol permeability of the membrane specimens were measured by a self-made diaphragm diffusion cell, which was closed to the one described in Ref [17]. The membranes were immersed in de-ionized water at room temperature for 24 h before tests, and both of the thickness and areas were measured. Thereafter, the membranes specimens were settled down at test temperature above 1h and then placed in diffusion cell for methanol permeability tests. 70 mL 5 mol/L methanol was poured into one side of the diffusion cell and equal volume de-ionized into the other. Magnetic stirrers were used in both compartments to ensure uniformity. Those peak areas were converted into methanol concentration in the compartment of de-ionized water according to calibration cure detailed in Ref. The methanol permeability coefficient was calculated by the second law of Fick's diffusion.

The thermal stability of membranes was evaluated by recording thermo-gravimetric (TG) traces in nitrogen atmosphere (Q500, TA Company, USA). Heating rate was 10 °C·min^{-1}, temperature ranged from 50 °C to 700 °C and specimen weight of 5±2 mg in the membrane form was used for recording TG traces.

3. RESULTS AND DISCUSSION

By far, SPEEK has been proved to be sulfonated successfully [19]. Comparing the curves in figure 2, there are identical with the absorption peaks appearing at 1640 cm^{-1}, 1220 cm^{-1}, 1110 cm^{-1}, 1010 cm^{-1} and 739 cm^{-1}. Where there existed a wide absorption peak at 3400 cm^{-1} corresponded to O-H band stretching vibration then we got degree of reduction was 23.7 % accordingly. The multiple absorption peaks between 2850 cm^{-1} and 3000 cm^{-1} corresponded to C-H stretching vibration. Absorption peaks at 1427 cm^{-1} and 1570 cm^{-1} were assigned to imidazole symmetric stretching vibration, 1060 cm^{-1} was B-F symmetric bending vibration of BF_4^-, 1170 cm^{-1} was N-C symmetric stretching vibration of aromatic rings and 667 cm^{-1} belonged to characteristic peaks of -Si-O-. Above all, it was confirmed that BF was successfully synthesized. Comparing B0500 and B1000 infrared spectra, it is indicated that the peak area of B1000 is larger than B0500 at 667cm^{-1} due to the Si-O characteristic absorption peak. But the C-H stretching vibration peaks of $-CH_2$ and $-CH_3$ in B0505 are higher than B1000 which prove that the grafting rate in B1000 membrane is higher than B0500.

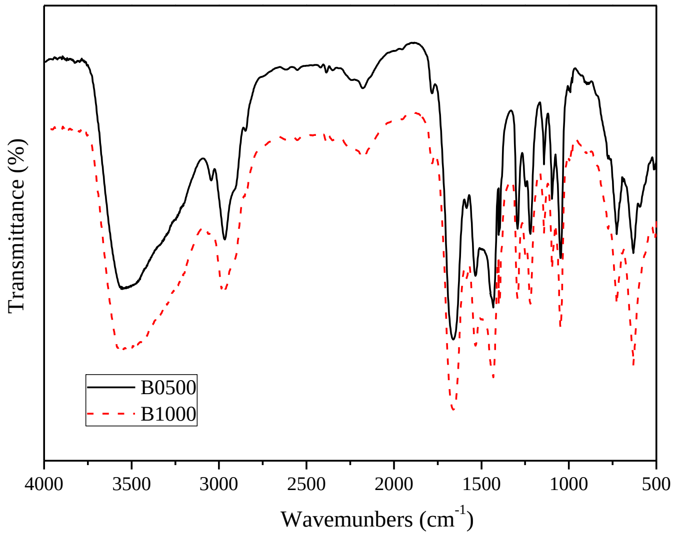

Figure 2. FT-IR spectra of imidazole tetrafluoroborate ionic liquid grafted SPEEK

Table 2 was the proton conductivity of SPEEK membrane and ionic liquids grafted SPEEK membranes at 30 °C. Proton conductivity increased than pure SPEEK by ionic liquids grafted, and an order of magnitude higher than pure SPEEK membrane which reached 10^{-2} S•cm^{-1}.

Table 2. Proton conductivity of SPEEK and grafted membranes at 30 °C

CODE	Thickness (cm)	Area (cm^2)	Impedance (Ω)	Proton conductivity (S·cm^{-1})
SPEEK	0.0079	0.1451	61.23	8.89×10^{-4}
B0500	0.0188	0.1451	22.33	5.80×10^{-3}
B1000	0.0196	0.1451	12.70	1.06×10^{-2}

The proton conductivity of the membranes as a function of temperature is shown in figure 3. As the temperature rising, the proton conductivity of the pure SPEEK membrane increased. The active participation of the proton transfer has been strengthened to improve the efficiency of their transitions in the membrane, resulting in proton conductivity increases. The proton conductivity of 64.5% DS pure SPEEK membrane was 1.82×10^{-4} S•cm^{-1} at 20 °C. But after grafted, all the proton conductivity increased to an order of magnitude than pure SPEEK membrane. And the membrane B1000 reached 10^{-2} S•cm^{-1} at 20 °C. Combined table 2, it reached a maximum 1.06×10^{-2} S•cm^{-1} at 90 °C. B0500 is up to 5.80×10^{-3} S•cm^{-1} at 90 °C. The proton conductivity of all the graft membranes reached 10^{-2} S•cm^{-1} at 90 °C. Due to the ions paired structure of ionic liquids with mobility which helps the proton conductivity in the membrane [20]. So, the proton conductivity of the membrane samples increases with temperature increasing.

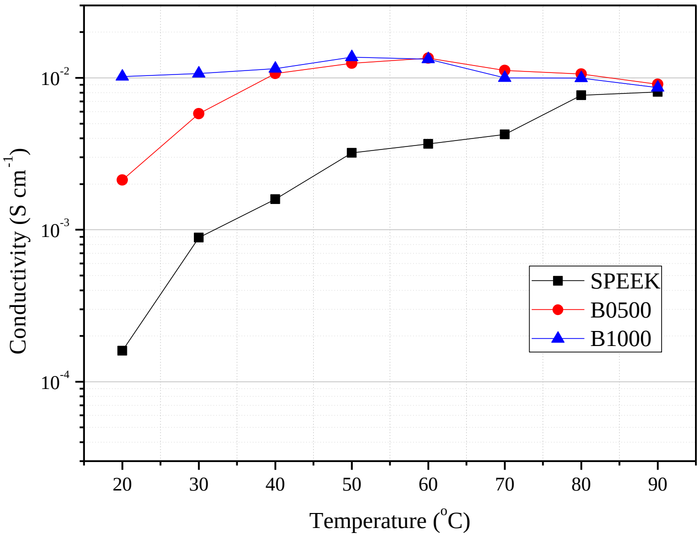

Figure 3. Proton conductivity of SPEEK and grafted membranes vs temperature

From the curves, it is indicated that the proton conductivity increased with the temperature increasing, wherein the proton conductivity of B1000 membrane was rather with pure SPEEK membrane and presents a more stable proton conductivity performance. The proton conductivity increases with the degree of grafting increasing. The proton conductivity of B1000 membrane was the best, reached 1.02×10^{-2} S•cm^{-1} at 20 °C, and arrived the highest 1.37×10^{-2} S•cm^{-1} at 50 °C. Infrared analysis also showed that there are hydrogen bonds in tetrafluoroborate ionic liquid with SPEEK to generate more dense structure, and easier transition after combining the proton and anion. The proton conductivity of B0500 rised firstly and then fell down, and arrived the highest 1.35×10^{-2} S•cm^{-1} at 60 °C which is higher than B1000 membrane.

At the same time, since B05 series had shown high proton conductivity, they were employed to continuously blend La_2O_3 for further modification. The proton conductivity of BF grafted and La_2O_3 doped SPEEK was show in figure 4. It is indicated that La_2O_3 wasn't beneficial to promote proton conductivity. With the increasing contents of La_2O_3, it reacted with sulfonic groups where generating coordination bonds each other. This effect finally led to amount of sulfonic groups cut down then hindered proton transportation in membranes since sulfonic groups acted as H^+ transportation.

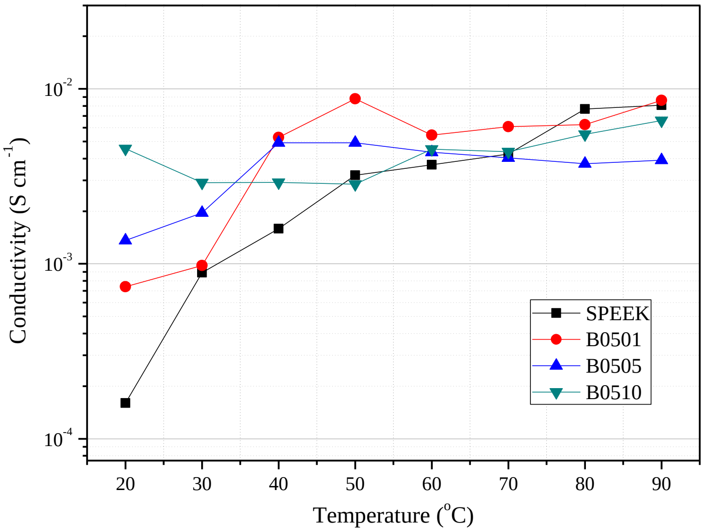

Figure 4. Proton conductivity of BF grafted and La_2O_3 doped SPEEK

Compared with B0501, the proton conductivity of B0505 membrane is much higher. Since protonated before the proton conductivity test of the samples, membrane samples are in acidic conditions. H^+ aggregated around La_2O_3 to help proton transfer between different sulfonic acid groups where a large number of H^+ environment, thereby improving the performance of the proton conductive membrane.

From figure 4, it is indicated that the proton conductivity of B0510 decreased significantly compared with B0505. This is because the hydrophilic groups were reduced with the La_2O_3 doping amount increasing. But the proton conductivity of the membrane is directly related to the content of the hydrophilic groups. That caused the reducing of proton conductivity. The proton conductivity of

B0510 membrane remained relatively stable varies with temperature and far below of B0505. In the low temperature region, the proton conductivity of the it is higher than that of pure SPEEK, such as the proton conductivity is up to 4.55×10^{-3} S•cm^{-1} at 20 °C, an order of magnitude higher than that of pure SPEEK at the same temperature. But at 90 °C, the proton conductivity of the membrane is reduced to 6.60×10^{-3} S•cm^{-1}, 82% of pure SPEEK membrane. That are probably due to the tetrafluoroborate ionic liquid has conductivity. SPEEK membrane has small number of activation protons at low temperature, the proton conductivity are mainly ionic liquid. Although membrane providing activation proton for migration are increased as the temperature rises, but due to excessive La_2O_3 content, the coordination reaction occurs between the sulfonic acid groups and La_2O_3 which caused the relative reduction in the number of sulfonic acid groups for proton conduction [21]. Thus, the proton conductivity of B0510 remained relatively stable with the temperature increasing.

Testing methanol permeability of the grafted SPEEK and different La_2O_3, doping content membranes to obtain methanol concentration versus time curve at get deionized water side which is shown in figure 5. The curves show that the methanol concentration of various osmotic membranes indicated a tendency to increase linearly with time, the slope of the curves are essentially the same as same that the methanol permeability coefficient substantially unchanged. The methanol permeation concentration of B1000 membrane water side was gradually increasing, methanol permeability increases and the increasing trend is most obvious. But the methanol permeation concentration of other four membranes did not exceed 10^{-2} mol/L^{-1} within 90 min, less different between the curves slope or methanol permeability coefficient. The reasons may be that the introduced tetrafluoroborate ionic liquid to form a water channel in the membrane, but a small number of it and did not cause a significant impact in the methanol permeation process. Therefore, the methanol concentration of crossover B0500 membrane is lower. But when increases tetrafluoroborate ionic liquid methanol, number of water permeable channels increased, so that methanol permeability concentration of B1000 membrane is maximum. The methanol permeability concentration of three membranes are substantially linearly increasing trend with the time increasing. While under the same infiltration time, all the methanol permeate concentration of water side of the membranes were decreased with the doping amount of yttrium oxide increasing. Rare earth metal oxide has a special structure and reactivity space [22]. When doped by La_2O_3, coordination reaction occurs at the electron-donating groups which are riched on SPEEK backbone and generated mutual attraction between sulfonic acid groups, reducing the number of sulfonic acid groups and blocking the methanol diffusion path, thus, reducing methanol permeation concentration of the modified membranes.

Obtained curves slope according to methanol permeation concentration versus time of pure water side, calculated methanol permeability coefficient according to the formula, as shown in Table 3. With the increase of La_2O_3, doping, methanol permeability coefficient appears a trend of rising after falling. It is probably due to the occurrence of interaction between La_2O_3, and ionic liquid. La_2O_3 are not uniformly dispersed in the membranes and the modification is not obvious. But with the increase amount of La_2O_3, doping, ionic liquids relative increase in the proportion of the membrane, lead to the methanol crossover intensified.

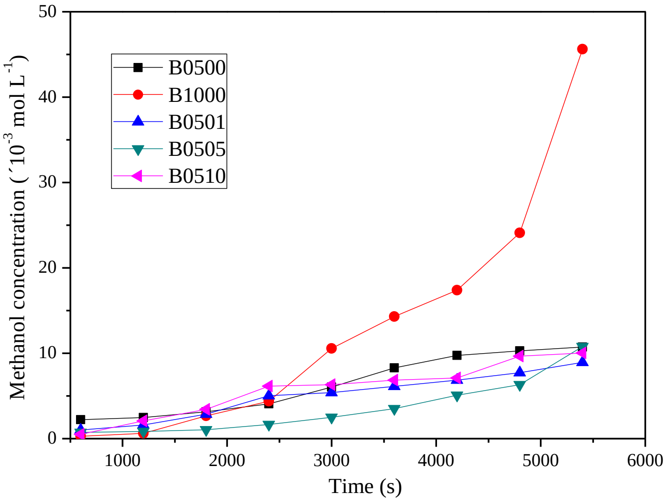

Figure 5. Methanol concentration of BF and La_2O_3 modified SPEEK membranes as a function of time

Table 3. Methanol permeability coefficient of SPEEK and grafted membranes

CODE	Thickness (cm)	Area (cm^2)	Straight Slope ($\times 10^{-6} mol \cdot L^{-1} \cdot s^{-1}$)	Methanol permeability coefficient ($\times 10^{-7} cm^2 \cdot s^{-1}$)
SPEEK	0.0077	0.3451	5.80	7.765
B0500	0.01885	0.3451	2.40	7.87
B1000	0.01155	0.3451	8.10	16.27
B0501	0.01688	0.3451	1.70	4.99
B0505	0.03370	0.3451	1.90	10.55
B0510	0.03528	0.3451	2.00	11.66

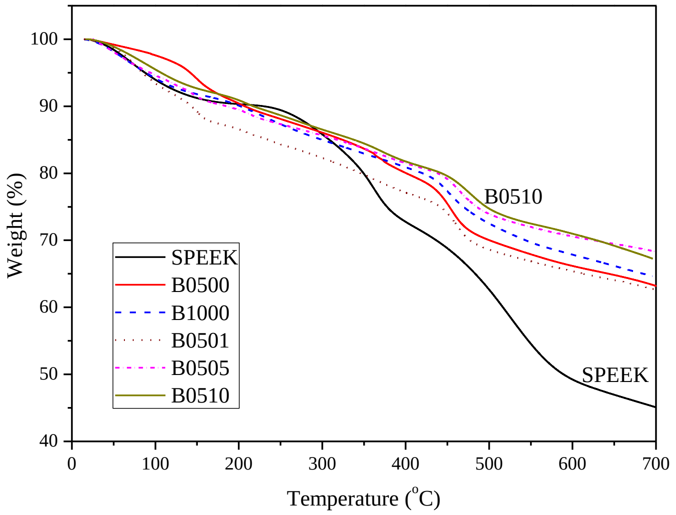

Figure 6. TG curves of BF and La_2O_3 modified SPEEK membranes

Thermo-gravimetric curves of BF and tetrafluoroborate ionic liquids grafted membrane are shown in figure 6. It is indicated that the thermal stability of the composite membranes slightly promoted with the increasing amount of doping La_2O_3. It is probably because that the reaction with ionic liquid or SPEEK corresponding groups to improve the compactness and stability of the membranes [23]. Thus, the thermal stability of B0510 is best.

4. CONCLUSIONS

Synthesized imidazole tetrafluoroborate ionic liquid (BF) to graft SPEEK proton exchange membrane and doped by La_2O_3, the grafting chemical structure of the membranes were validated by FTIR analysis. BF can significantly improve the proton conductivity and methanol concentration of the composite membranes. Comparing ordinary physical doping, chemical graft could effectively avoid the loss of ionic liquid and extend the using life of membranes. The proton conductivity of B0505 membrane arrived 4×10^{-2} S•cm^{-1} after doped by La_2O_3. But the B0501 membrane has the highest methanol concentration upon 10^{-6} cm$^{2}\cdot$s^{-1} which is higher than pure SPEEK. When doped by La_2O_3, coordination reaction occurs at the electron-donating groups which are riched on SPEEK backbone and generated mutual attraction between sulfonic acid groups, reducing the number of sulfonic acid groups and blocking the methanol diffusion path, thus, reducing methanol permeation concentration of the modified membranes. The thermal stability of grafted membranes is higher than pure SPEEK which is attributed to the chemical bond energy.

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