Hindawi
Advances in Materials Science and Engineering
Volume 2022, Article ID 2796802, 14 pages
https://doi.org/10.1155/2022/2796802

*Research Article*

# Preparation and Electrochemical Performance Analysis of Flexible Ionic Polymers by Freeze-Drying Technology

**Jintao Zhao, Junpeng Shao, Zhenjie Zhang, Bo Liang, Mingchao Yuan, and Hanyu Wang**

*School of Mechanical and Power Engineering, Harbin University of Science and Technology, No. 52 Xuefu Road, Nangang District, Harbin 150080, Heilongjiang, China*

Correspondence should be addressed to Zhenjie Zhang; dml345@hrbust.edu.cn and Bo Liang; liangbo_hrbust@163.com

Received 22 April 2022; Revised 21 November 2022; Accepted 26 November 2022; Published 12 December 2022

Academic Editor: Isabel J. Ferrer



With the development of bionics and marine science, a new artificial muscle material, IPMC (ion-exchange polymer metal composite), has attracted significant attention. However, the performance issues, as well as problems associated with the preparation of IPMC, have limited its development. In this study, we use the freeze-drying technique, successfully creating a new type of enhanced carbon nanotube IPMC material. Moreover, we also use the method of cyclic voltammetry, ac impedance, and the constant current charge and discharge method to analyze and evaluate the multiwalled carbon nanotube (MWCNT)-reinforced IPMC produced by freeze-drying technology. Freeze-dried IPMC has a higher moisture content, which is 1.58 times higher than that of ordinary IPMC. The pore and multiwalled carbon nanotube (MWCNT) in the ion exchange membrane are distributed more homogeneously. The technology prepared by IPMC has superior electrical performance. Under a 2 v scanning interval and a scanning speed of 50 mV/s, its specific capacitance can reach 247.5335 mF/cm$^{-2}$, which is 24 times that of normal IPMC. Under the same conditions, its conductivity can reach 0.29391 mS/cm, far higher than that of ordinary IPMC. Furthermore, the preparation process is also safer. This method provides a new strategy for the future preparation and usage of IPMC.

## 1. Introduction

With the continuous development of bionic and intelligent materials, ionic polymer metal composites (IPMC) have attracted the attention of researchers because of their special features, and bionic IPMC artificial muscles are gradually formed, and flexible materials gradually enter people's lives [1–4]. IPMC is a type of lightweight, high-flexibility electroactive material (EM). It is composed of an ion exchange membrane and a metal electrode plating on the sides of the ion exchange membrane. Under the condition of electricity, this type of IPMC can generate large deformation; under an external load, it also can produce an induced current, because its structure has a large specific surface area and high electrical performance. Compared with shape memory alloys and piezoelectric ceramic materials, IPMC not only has a more compact and simpler structure but also has a faster response speed and a stronger deformation ability. Moreover, because IPMC has unique sensing properties, it is widely used in software robots, sensors, and the medical field, to simplify mechanical structures or improve the efficiency of energy conversion, and it still has very broad prospects [5–7].

Although IPMC has excellent performance and special functions, in practice, there are still many limitations, such as the high water sensitivity—its action will decrease in a dry environment—and the smaller output force and short service life, and its output capacity is related to thickness [8]. IPMC is easy to fail; in the period of time after its use, IPMC will lose its activity, and at the same time, there will be many irreversible changes in its structure, and it will lose its effectiveness of motion. Secondly, the preparation of IPMC is more complex and expensive, and it is thus not currently suitable for wide use; to this end, researchers who are studying its preparation hope to be able to improve the performance or reduce the production cost of IPMC. There are also researchers who optimize IPMC driving and sensing capabilities through control algorithms [9, 10].

In fact, the middle part of IPMC is a polymer membrane, which can promote ion exchange [11, 12], IPMC's output force is smaller and its ion exchange membrane can easily break, so many researchers seek to enhance the performance of IPMC with reinforced material in the ion exchange membrane. There are also many researchers looking for new molding processes, such as the hydrogel printing technology researched by Hong Chen and others [13].

Researchers have incorporated MWCNTs into the membrane, enhancing the intensity of the ion exchange membrane. In 2015 [14], Hao doped MWCNTs in a Nafion solution, creating a new type of MWCNT/IPMC material. The IPMC's resistance was significantly reduced, and the maximum output force compared with the traditional IPMC increased by 14.84%, making IPMCs more suitable in the field of medical and industrial applications. Therefore, using an appropriate reinforced material can improve the performance of IPMC.

In previous studies, researchers found that the performance of IPMC is associated with its specific capacitance and conductivity. Wu et al. measured the electrochemical properties of helical IPMC and found that its properties were closely related to mechanical properties [15]. Sun [16] analyzed an IPMC MWCNT/$MnO_2$ composite electrode, and proved that the IPMC's capacitor, the output power density, specific capacitance, and the changing trend of strain are basically identical; they also found that the performance of IPMC is related to the content of MWCNT and $MnO_2$. He found that the chitosan membrane had good biocompatibility. This finding was consistent with that of Ahmed Madni et al. [17]. From this experiment, we can also learn that the performance of IPMC in relation to specific capacitance and other related parameters is large; at the same time, we can see that the influence of the electrode material of IPMC is also large. For metal electrodes, the metal electrode layer resistance value is smaller, and IPMC has higher performance. Currently, we use Pt and Au metals as the electrode layer as their resistance is usually very low. However, these two metals are very expensive; using an electroless plating electrode, the price of the salt solution is also very high, leading to the costly preparation of IPMC. In this article, we use silver as the electrode layer. Although silver cannot compare with Pt and Au as the electrode layer, its price is much lower.

Furthermore, compared with copper, silver's performance is superior, and the price gap is not large. Compared with previous researchers, we can see that the traditional IPMC uses a Nafion membrane as the basement membrane, and uses different technologies for the electrode coating on both sides of the membrane, the performance of IPMC is related to the ion exchange membrane and metal electrode layer. The higher the electrode quality, the better the performance of IPMC [18–20]. The commonly used electrode plating processes can be divided into chemical plating and hot pressing. The electrode layer produced by chemical plating, combined tightly with an ion exchange membrane, does not easily fall off, but the resistance is large and the price is very high since, in order to improve the electrode layer's density, this step needs to be repeated [21]. Moreover, if we add different reinforced materials in the ion exchange membrane, we also can improve the performance of IPMC; for example, graphene oxide can improve the conductivity, electric capacity, and energy storage [22, 23].

Therefore researchers often use casting of the ion exchange membrane prepared by the solution such as Nafion D520 solution is mixed with the reinforced material, in a particular container, to produce an evaporation film. In order to adjust the evaporation rate in the process of evaporation, we often incorporate dimethyl sulfoxide, dimethyl acetamide, or flammable toxic organic compounds. The film-forming process can produce poisonous gases, which pose risks to human health. Thus, in this study, we hope to improve the performance of IPMC and its preparation process and consequently reduce IPMC's risks to the human body.

The doping modification of the IPMC ion exchange membrane can improve the mechanical properties of IPMC and promote ion conduction. The porous modification of the IPMC ion exchange membrane can improve the water content of IPMC. We found that carbon nanotube is a one-dimensional quantum material with a special structure. MWCNTs are light in weight, perfectly connected in a hexagonal structure, and have many unusual mechanical, electrical, and chemical properties. Khan et al. found that this material greatly improved energy storage and prepared high-performance supercapacitors [24–26]. Therefore, we added MWCNT to the ion exchange membrane as a reinforcing material. We hope that MWCNT can improve the mechanical and electrical properties of IPMC. We also hope to reduce the effect of poor material strength due to porous structure and improve the performance of IPMC.

## 2. Materials and Methods

*2.1. Experimental Materials.* This experiment mainly used the following materials: Nafion D520 solution, from the United States DuPont; MWCNTs from ZhaoYe New Material Co., Ltd.; zinc oxide powder, from the National Medicine Group Chemical Reagent Co., Ltd.; dimethyl sulfoxide, from the National Medicine Group Chemical Reagent Co., Ltd.; silver nitrate, from the TianJin branch of the Chemical Reagent Co., Ltd.; ammonia, from the TianJin branch of the Chemical Reagent Co., Ltd., and glucose powder, from the National Medicine Group Chemical Reagent co., Ltd.

*2.2. Technological Method.* We produced and tested a variety of IPMCs. In order to reduce the test link and the clamping effect on the properties of IPMC for subsequent testing, we decided to use an electrochemical workstation first to perform the cyclic voltammetry test and ac impedance test; we then exported data as CV curves and EIS curves. Next, we used blue electric batteries in the system to perform the constant current charging and discharging experiments of IPMC and draw the GCD curve, eventually using an electronic balance and vacuum drying oven to perform the water loss test.

*2.3. Technological Process.* The process flow of IPMC involves membrane pouring, coarsening, and electrode preparation. The size of the ion exchange membrane, appearance posture, the content of materials as well as the selection and preparation of the electrode process will affect the various properties of IPMC, so they need to be controlled in the process of preparation through various variables [27]. Thus, in our research, we selected various variables, using the solution casting method to design the 5 types of IPMC.

Three types of IPMC were produced by heating in this study. These were IPMCs with a carbon nanotube mass fraction of 0.5%, ordinary IPMCs, and porous IPMCs. Then, two types of IPMC were prepared with the use of freeze-drying technology, namely, ordinary IPMC and IPMC with a carbon nanotube mass fraction of 0.5%. Then, in the comparative experiment, looking for the differences, the five types of IPMC were prepared with a silver electrode; using the electroless plating method, each IPMC was subjected to many chemical plating steps, to reduce the influence of the electrode on the IPMC's performance. The dry heating preparation process is shown in Figure 1. The freeze-drying steps are shown in Figure 2.

## 3. Results and Discussion

*3.1. SEM Analysis.* Figure 3 shows the SEM images of five IPMCs. From the figure, we can see the internal shape of the ion exchange membrane. Compared with the porous IPMC prepared by heating and drying and the two IPMC prepared by the freeze drying process, it can be observed that the shape of the two is similar, which means that there are pores in the ordinary IPMC subjected to freeze drying, and also indicates the feasibility of preparing porous membranes through the freeze drying process. As shown in the diagram, the tablet analysis demonstrated that in the porous IPMC, pores for heating and drying are concentrated on one side, while the pores of the IPMC prepared by the freezing and drying process are relatively uniform. This is because ordinary porous IPMCs are prepared by particle leaching. Although there are many vibrations in the preparation process, ZnO still produced partial precipitation, resulting in ions. The exchange membrane is uneven; two types of ion exchange membranes containing MWCNT were observed. The IPMC containing MWCNT enhanced by the freeze-drying method obviously had some pores, and the pores were evenly dispersed from MWCNT. These phenomena verify the feasibility of preparing IPMC by freeze drying, and the freeze drying process does not require the heating of toxic reagents such as DMSO, which improves the safety of the preparation process.

The five IPMCs in Figure 3 all contain voids. These voids will make IPMC ion exchange membrane store water, and higher water content can improve the performance of IPMC. The IPMC in Figure 3(a) has few voids, which will affect the water content of the IPMC. The holes in IPMC will affect the mechanical strength of the ion exchange membrane. If there are too many holes in the ion exchange membrane, the exchange membrane is more likely to break. After MWCNT was added to IPMC, the materials inside the membrane were closely related to each other and the mechanical properties were enhanced. We can see that the IPMC in Figures 3(b) and 3(e) have a large number of MWCNTs. These MWCNTs will fill the voids in some ion exchange membranes and reduce the water content. But MWCNT can improve the conductivity of the ion exchange membrane and improve the mechanical strength of the ion exchange membrane.

*3.2. CV Test Analysis.* The cyclic voltammetry controls the potential of the charged electrode at different speeds and scans repeatedly in a triangular waveform over time. The potential range enables different redox reactions on the electrode to take place alternately and records the change in current and voltage. The curve formed by the current and voltage is the CV curve. The area enclosed by the CV Curve is the capacitance. The ratio of the capacitance to the area of the IPMC is the specific capacitance.

In this study, an electrochemical workstation was used to analyze the CV of the five IPMCs, and 1 mol/L $Na_2SO_4$ solution was used as the electrolyte. The five IPMCs were scanned cyclically at the speeds of 50 mv/s, 100 mv/s, 200 mv/s, and 500 mv/s. The scanning interval was set as −1 V-0 V and −1 V–1 V, and cycles were repeated many times to achieve stable data export processing. The processed CV curve with a scanning range of −1 V-0 V is shown in Figure 4.

Because the gap between the CV curves containing MWCNT and those without MWCNT is too large in the case of −1 V to 1 V, the classification was made, as shown in Figures 5 and 6, compared with the specific capacitance shown in Figure 7.

In Figure 4, it can be seen that the movement trend of several IPMCs is roughly the same. The specific capacitance of the two types of MWCNTs is much higher than that of the other three. It can be seen in Figure 4 that the movement trend of several IPMCs is roughly the same, indicating that these groups of IPMCs have stable conductivity. Among them, there are slight fluctuations in the lyophilized ordinary membrane, which is mainly related to whether the electrolyte membrane is uniform [28]. It can be suggested that there are two reasons for this situation.

(1) The ion exchange membrane was prepared by the freeze-drying process. The solvent in the ion exchange membrane of IPMC can be evaporated directly by freeze-drying technology. There will be some holes in the middle of the prepared IPMC's ion membrane, and the texture of the ion exchange membrane will not be uniform.

(2) The electrode coating was uneven and not firm. The electrode plating is closely related to the coarsening of the ion exchange membrane. The holes in the ion exchange membrane change the mechanical properties and poor toughness of IPMC. Compared with the ion exchange membrane prepared by the heating and drying process, it is more prone to fracture. Moreover, the IPMC ion exchange membrane prepared in this study was very thin and only floated up

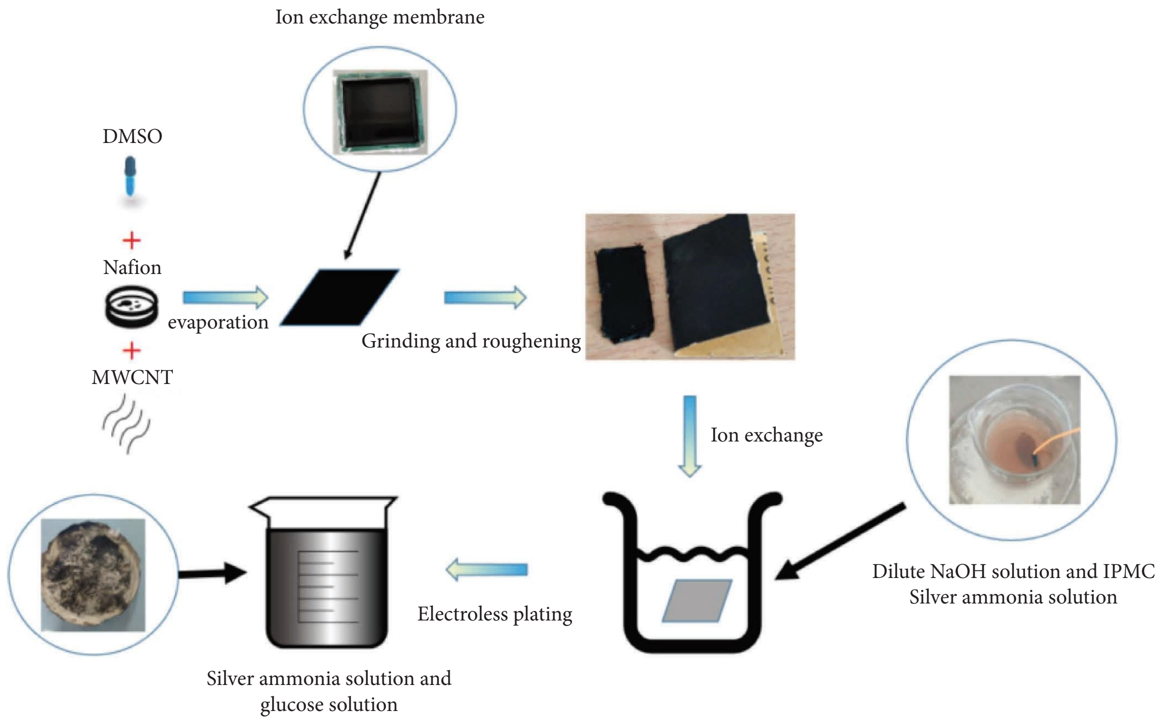


Figure 1: Dry heating preparation process.

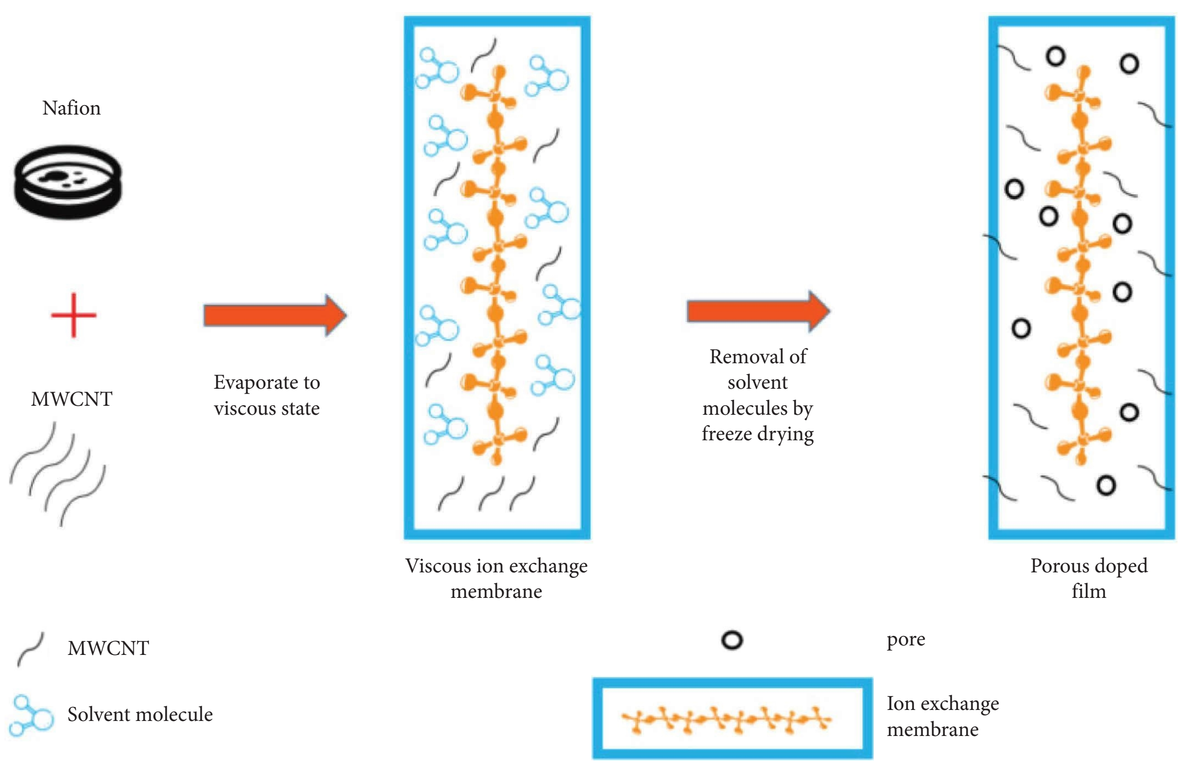


Figure 2: Freeze drying.

and down at a thickness of 0.2 mm. The coarsening process of freeze-dried IPMC was difficult. Under the same coarsening and grinding times, the coarsening effect of freeze-dried IPMC was worse than that of the ion exchange membrane prepared by heating and drying, resulting in a poor electrode plating effect of IPMC. During the IPMC test, some electrode layers on the surface fall off. Therefore, the CV curve of IPMC prepared by freeze-drying technology fluctuated slightly.

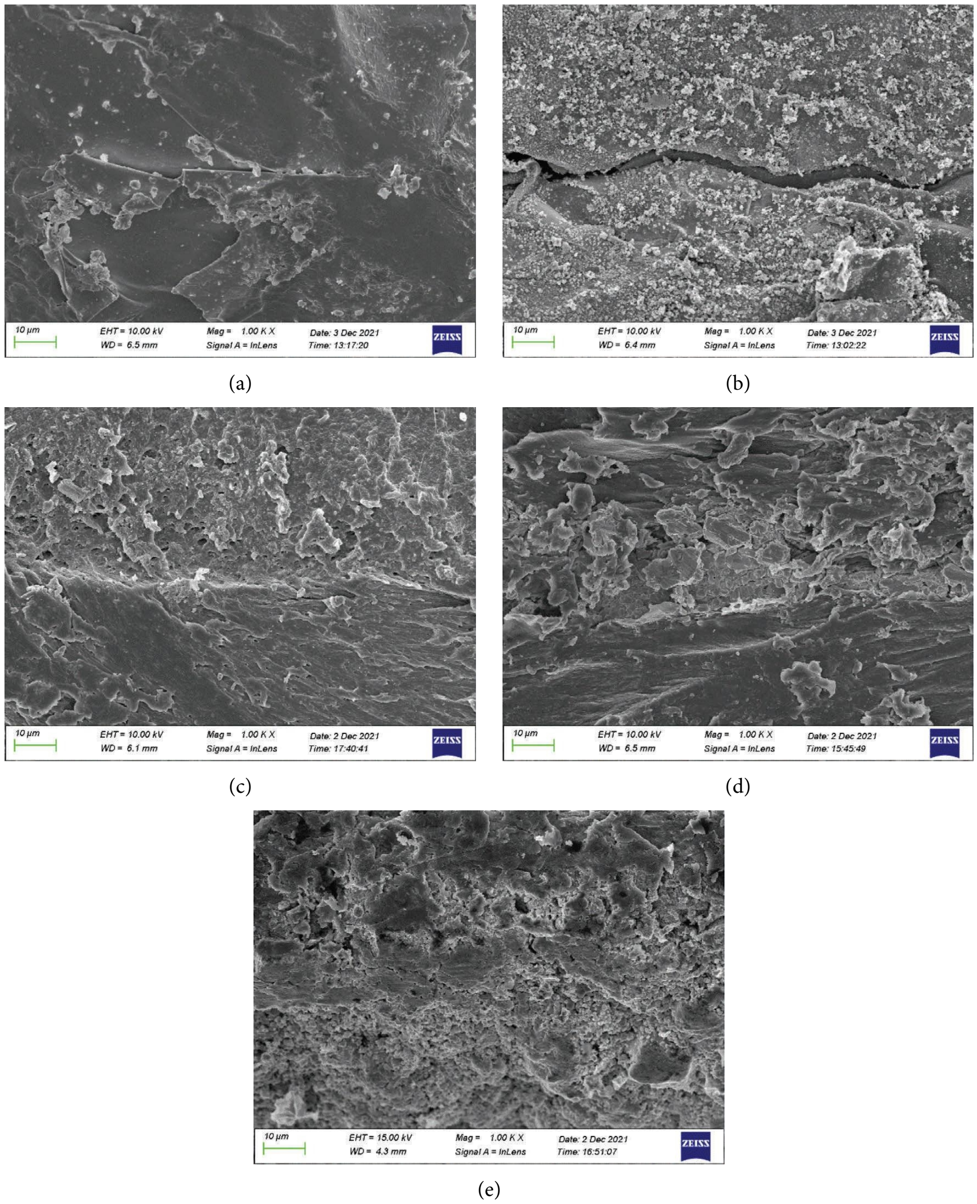


Figure 3: SEM figure: (a) SEM of common IPMC; (b) SEM of MWCNT-enhanced IPMC; (c) SEM of ordinary porous IPMC; (d) SEM of freeze-dried common IPMC; (e) SEM of freeze-dried MWCNT-reinforced IPMC.

It can be seen in Figure 4 that the specific capacitance of the IPMC prepared by freeze-drying technology is very large. The IPMC test piece containing MWCNTs prepared by freeze-drying technology contains a large number of MWCNTs as reinforcing materials, which improves the mechanical properties and coarsening effect of IPMC. At the same time, there are many MWCNTs on the surface of the IPMC ion exchange membrane, which can improve the surface roughness of the ion exchange membrane. The exposed MWCNT provides a large number of contacts for the precipitation growth of electroless-plated silver, further improving the electrode's adhesion ability. In addition, the membrane prepared by the freeze-drying process has higher water content, and, because of the hydrated cation driving principle of IPMC, an IPMC with greater water content has better performance. Therefore, the specific capacitance of the IPMC prepared by the freeze-drying process containing MWCNTs is greater than that of conventional IPMC. It can be seen from the table that, with an increase in scanning rate, the specific capacitance gradually decreases. This is because, with an increase in the scanning interval, the ion channel does not increase and the ion diffusion rate remains unchanged, so the specific capacitance decreases.

It can also be seen in Figure 4 that the area enclosed by the CV curves of the two types of MWCNTs is much higher than that of the other three types. This is because, after the addition of MWCNTs, the internal conductivity of the IPMC membrane is improved, the surface area of the MWCNTs is large, the inner wall provides a large number of water molecules and ion channels for the interior of the

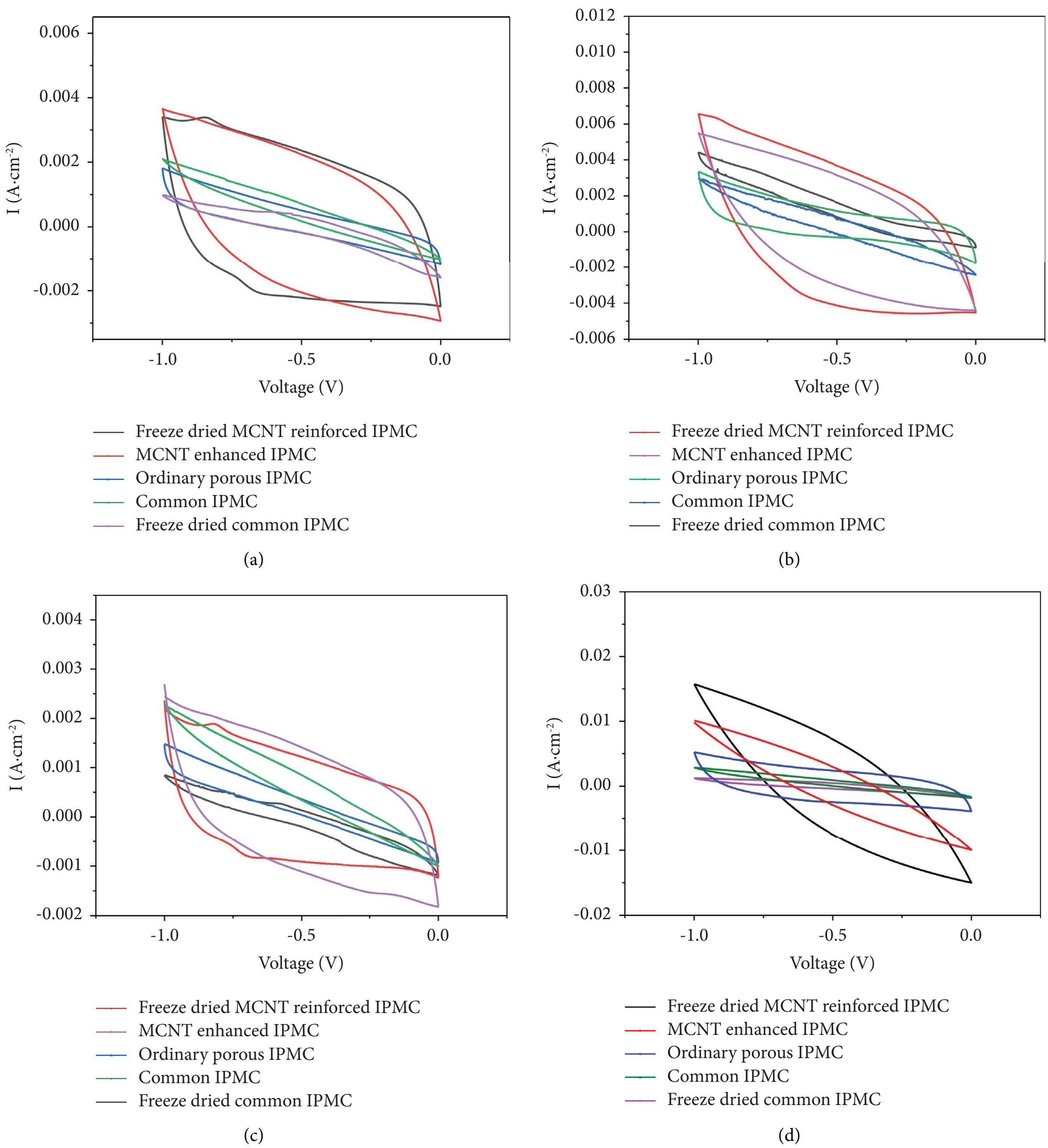


Figure 4: CV diagram with scanning interval of −1 v-0 v and different scanning speeds: (a) 50 mV/s; (b) 100 mV/s; (c) 200 mV/s; (d) 500 mV/s.

membrane, and the wall of the MWCNTS has good conductivity. Carbon nanotube walls can provide electron passage and store more charge [29].

The specific capacitance of the IPMC ion exchange membrane has a significant relationship with the electrode. First, after adding MWCNTs, there will be attachment points on the surface of the IPMC ion exchange membrane, which makes the electrode plating effect better, resulting in better electrochemical performance. Second, MWCNTs are in the form of nanostructures, which have the advantages of large specific surface area and appropriate pore size, increasing the effective surface area of the electrode and demonstrating good conductivity [30]. Some MWCNTs on the surface of the ion exchange membrane form a good interface layer with the plated metal silver and the metal silver entering the membrane during the ion exchange process, which has good conductivity. It can store a large number of electrons, improve the electrode quality further, and improve the specific capacitance performance of IPMC.

From Figures 5 and 6, it can be seen that the performance of the IPMC containing MWCNTs is significantly improved. The graphics in Figure 6 also show that some changes took place, and it can be seen that, for the membrane containing MWCNTs, the Redox peak appeared more obvious than

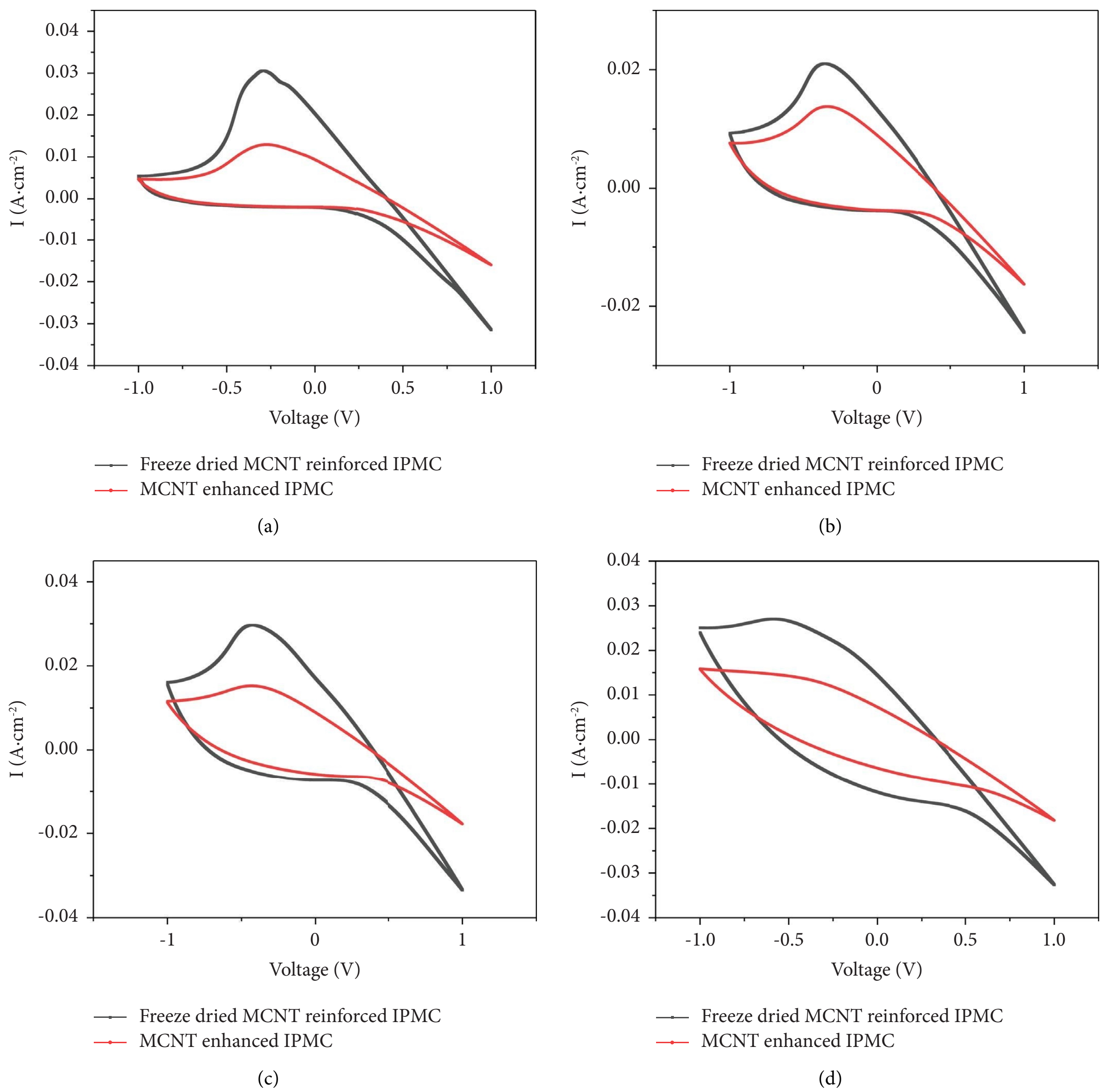


Figure 5: CV diagram of IPMC containing carbon nanotubes with a scanning interval of −1 V–1 V: (a) 50 mV/s; (b) 100 mV/s; (c) 200 mV/s; (d) 500 mV/s.

before, which is due in part to impurities in the silver oxide layer and membrane on the surface when the Redox reaction happens, leading to an irreversible reaction and forming a reduction peak, so that, in the following scan, the IPMC reduction summit decreases. This indicates that the silver oxide electrode layer on the surface is gradually reduced and the reaction is irreversible. When the scanning interval is small, it will charge into IPMC first. When it is not full, the Redox reaction is not violent, so the reduction peak cannot be seen when the scanning interval is −1 V-0 V. However, the reduction peak of the film without any modification and prepared by hot drying and freeze-drying is very small because the mechanical properties of the two films mentioned above lead to a general coarsening effect. In the case of the same number of plating steps, the surface electrode's quality is poor, the silver content is low, and the silver oxide generation is low. After repeated scanning under the same scanning conditions, the reduction peak becomes very small. The porous IPMC prepared by heating and drying will produce a large Redox peak because the porous surface will increase the friction force and the contact area between the silver electrode and the ion exchange film, resulting in better electrode quality. In addition, due to the thin electrode layer, the contact area between the electrode and the air is larger, and more silver oxide is formed. This is also the reason that the ordinary IPMC prepared by Freeze drying Technology still has a small Redox peak under the condition of 0.1 scanning speed, but the reduction peak of the IPMC prepared by heating and drying has disappeared.

Compared with several IPMCs without MWCNTs, it can be seen that the effect of porous IPMC with zinc oxide is better. This is because the porous structure in the film

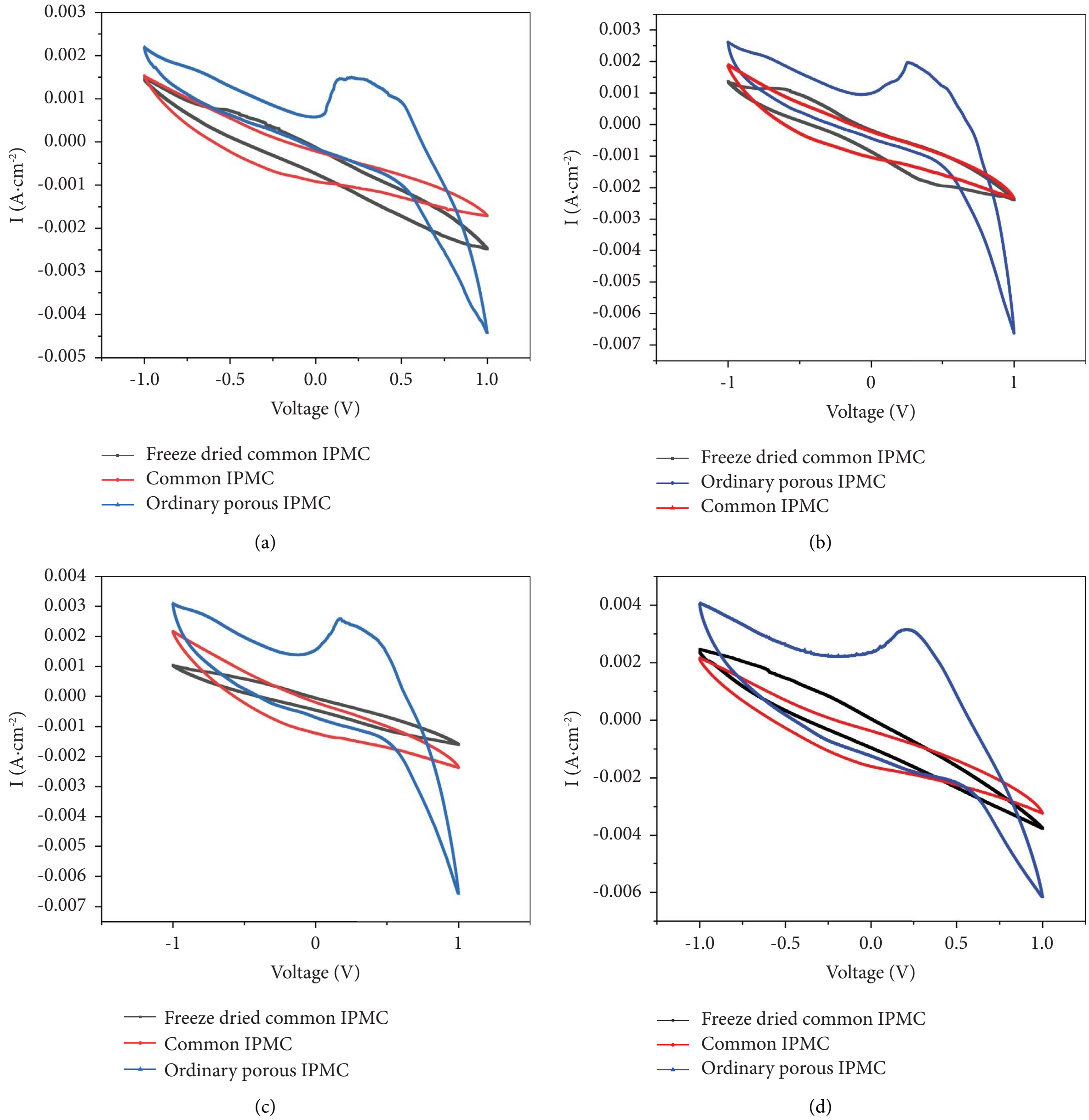


Figure 6: The scanning range of IPMC without carbon nanotubes is −1 V–1 V CV: (a) 50 mV/s; (b) 100 mV/s; (c) 200 mV/s; (d) 500 mV/s.

increases the contact area between the film and the electrode, which improves the effective area of the electrode and the water content in the film.

In conclusion, IPMC-reinforced with MWCNTs prepared by freeze-drying technology has the largest specific capacitance, which not only solves the problem of poor electrode quality caused by the coarsening problem of ordinary freeze-dried IPMC but also greatly improves the performance of IPMC.

*3.3. AC Impedance Test (EIS).* Electrochemical impedance spectroscopy (EIS) is a nondestructive type of parameter measurement that uses the small-amplitude sinusoidal potential (or current) as the disturbance signal to generate an approximate linear response of the electrode system, and measures the impedance spectrum of the electrode system in a wide frequency range, so as to study the IPMC system [31, 32]. In this experiment, 1 mol/L $Na_2SO_4$ electrolyte solution was used to measure the AC impedance spectrum of the sample between 0.01 Hz and 5104 Hz. After this, we used Z-view software and the equivalent circuit in the figure to fit the data, and we obtained Figure 8, where the equivalent resistance Re reflects the implementation of the overall internal resistance. With the *X*-axis intersection curve of the high-frequency region, we obtained the Rct for the electrode materials with electrolytes used in the test of the contact surface. Moreover, the Faraday reaction occurred, hindering the charge transfer resistance. The conductivity formula is shown in the figure below, where *L* is the thickness of IPMC, A is the effective area, and *R* is the ohmic resistance, which can be obtained from the fitting curve. The fitting curve

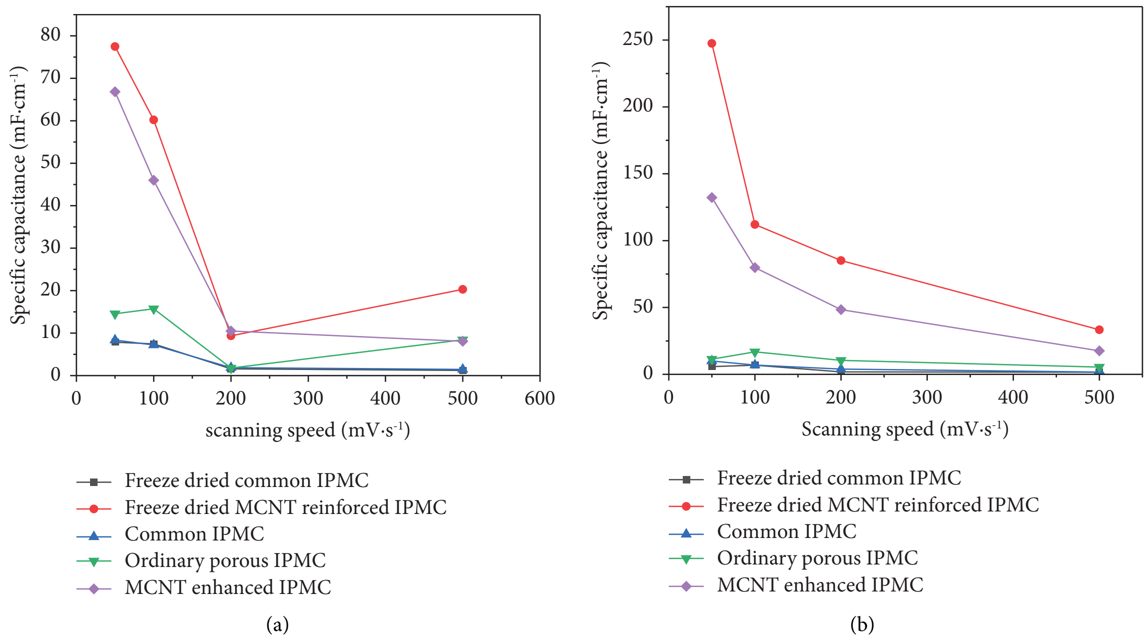


FIGURE 7: Comparison of specific capacitance in different scanning intervals: (a) −1 V-0 V; (b) −1 V–1 V.

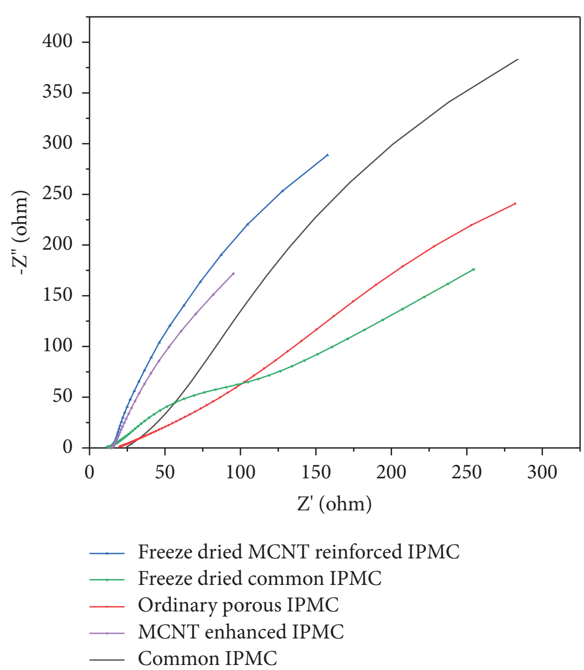


FIGURE 8: EIS curve.

finally obtained is shown in Figure 8. The ionic conductivity results for IPMC with different parameters and various parameters obtained by fit-ting are shown in Table 1.

As can be seen from Figure 8 and Table 1, the conductivity and capacitance of IPMC with MWCNT are significantly improved. The equivalent resistance of the equivalent circuit is reduced because the MWCNT in the ion exchange membrane can form ion channels and electron pathways, which reduces the equivalent total resistance of IPMC. The resistance of the two types of freeze-dried IPMC decreased by different amplitudes compared with that of the heating-dried IPMC. This is because the IPMC prepared by freeze-drying technology has higher water content, which leads to a reduction in resistance. The same is true for the resistance of the porous film prepared by heating dried IPMC.

Compared with several transfer resistors, the resistance of the two types of IPMC containing MWCNTs is significantly smaller, followed by that of ordinary porous IPMC and then the two types of ordinary unmodified IPMC, which

Table 1: Fitting parameters.

| Type | Common IPMC | Ordinary porous IPMC | MWCNT-enhanced IPMC | Freeze-dried common IPMC | Freeze-dried MWCNT-reinforced IPMC |
|---|---|---|---|---|---|
| Rct (Ω) | 670.8 | 204.7 | 71.61 | 624.1 | 35.46 |
| Re (Ω) | 23.42 | 15.82 | 13.98 | 9.967 | 11.9 |
| C (mF) | 6.0782 | 8.892 | 264.67 | 7.1232 | 41.065 |
| Electrical conductivity (mS/cm) | 0.05887 | 0.10065 | 0.17447 | 0.06313 | 0.29391 |

is greatly related to the electrode of IPMC. Under the same conditions and the same number of electroless plating steps, the performance of the two types of IPMC electrodes containing MWCNTs will be better. However, only the IPMC prepared by freeze-drying had a poor effect, which is the same as in the previous analysis.

By comparing the capacitors of several IPMCs, it can be found that the capacitors containing MWCNTs are relatively high. This is because MWCNTs are tiny tubes that can store a large number of electrons. A large number of MWCNTs in the membrane improves the specific area in the membrane, which leads to an increase in the capacitance of IPMC. Freeze-drying preparation of the IPMC membrane due to its porous structure causes the membrane water content and permeability to increase, and also allows them to be lost more easily; at the same time, when the IPMC is used as an actuator or sensor, it should have a faster response speed; in addition, the freeze drying preparation of IPMC will result in an evenly mixed solution that is quickly frozen. Compared with dry heating, the rapid freezing process will cause the MWCNTs to be evenly dispersed in the film, and the ion channel formed after the film will be more uniform, which will improve the ion diffusion rate. Meanwhile, the agglomeration effect and precipitation effect are reduced, which will make the osmotic pressure of IPMC more uniform, and the IPMC prepared will have better performance.

*3.4. Constant Current Charge and Discharge Test and Analysis.* A blue battery test system was used in the experiment. Here, 1 mol/L $Na_2SO_4$ solution was used as the electrolyte solution. The cycle time was set to 10 S and 30 S, the charging current was set to 1 mA and 1.5 mA, and the protection voltage was set to 3 V and 5 V. The average mass value of IPMC electroactive substance can be estimated to be approximately 0.1 A/g and 0.15 A/g. Each group was cycled 100 times, and one group of stable curves was cut and drawn, as shown in Figure 9. Voltage drop and capacitance retention are shown in Figure 10.

It can be clearly seen from Figures 9 and 10 that the voltage drop of each IPMC shows an increasing trend with the increase in the test current, which indicates that the internal resistance increases significantly with the increase in current density. Meanwhile, it can be seen from the figure that the internal resistance of the two IPMCs with MWCNTs is significantly smaller, which is also the same as the previous conclusion. By comparing several IPMCs without MWCNTs, it is found that the variation law of voltage drop and internal resistance is similar, and the specific capacitance law is similar to that obtained in CV above. It can be clearly seen in the figure and the table that the performance of the IPMC prepared by freeze drying changes dramatically in the case of a 30-second cycle of 1.5 mA. This is partly because, when the current density is increased and the protection voltage is adjusted, the upper limit is higher and various internal resistance properties of IPMC are more easily highlighted. At the same time, the IPMC electrode prepared by freeze-drying technology has a poorer coating condition. After several cycles of experiments, the surface electrode falls off, resulting in a sudden increase in resistance. A comparison of two different cycle curves clearly indicates that, when the cycle is longer, the curve slows, with different degrees of lower voltage drop at the same time. Several types of IPMC gaps can be more easily observed in the long-term 1 mA charging cycle at the same time. Several types of voltage drop occur, where the porous IPMC's voltage drop will be even less than that of the carbon IPMC when the current increases. It is speculated that the reason for this phenomenon is related to the size of the IPMC. The size of the IPMC prepared in this study was not completely consistent, and the part under the liquid level was not completely consistent during the test, leading to differences in charging capacity.

We present the capacitance retention rate of several specimens after multiple cycles in Figure 10. The capacitance retention rate is the ratio of the cyclic capacity of IPMC to its initial capacity after multiple cycles. Thus, it can replace IPMC approximation in circulation after many cycles of capacitance capacity and after the service life of the IPMC, when the poor quality of the electrode and electrode loss will affect its performance. It is clear that freeze-drying technology during the preparation of ordinary IPMC leads to poor performance, but, after the incorporation of MWCNTs with many arms, the performance can be significantly enhanced. Similar to the above analysis, this is also because the freeze-drying technology enables MWCNTs to be evenly dispersed in the film, which improves the performance of IPMC and solves the problem of the poor mechanical properties of freeze-dried IPMC.

*3.5. Moisture Content Test and Analysis.* Due to the hydrophilicity and hydration cationic driving principle of IPMC, the moisture content of IPMC has a great influence on its performance, so it was necessary to conduct a moisture content test of the studied IPMCs. The IPMC after the previous test was stored in water for one day so that it could absorb water fully. After it was removed, the distilled water

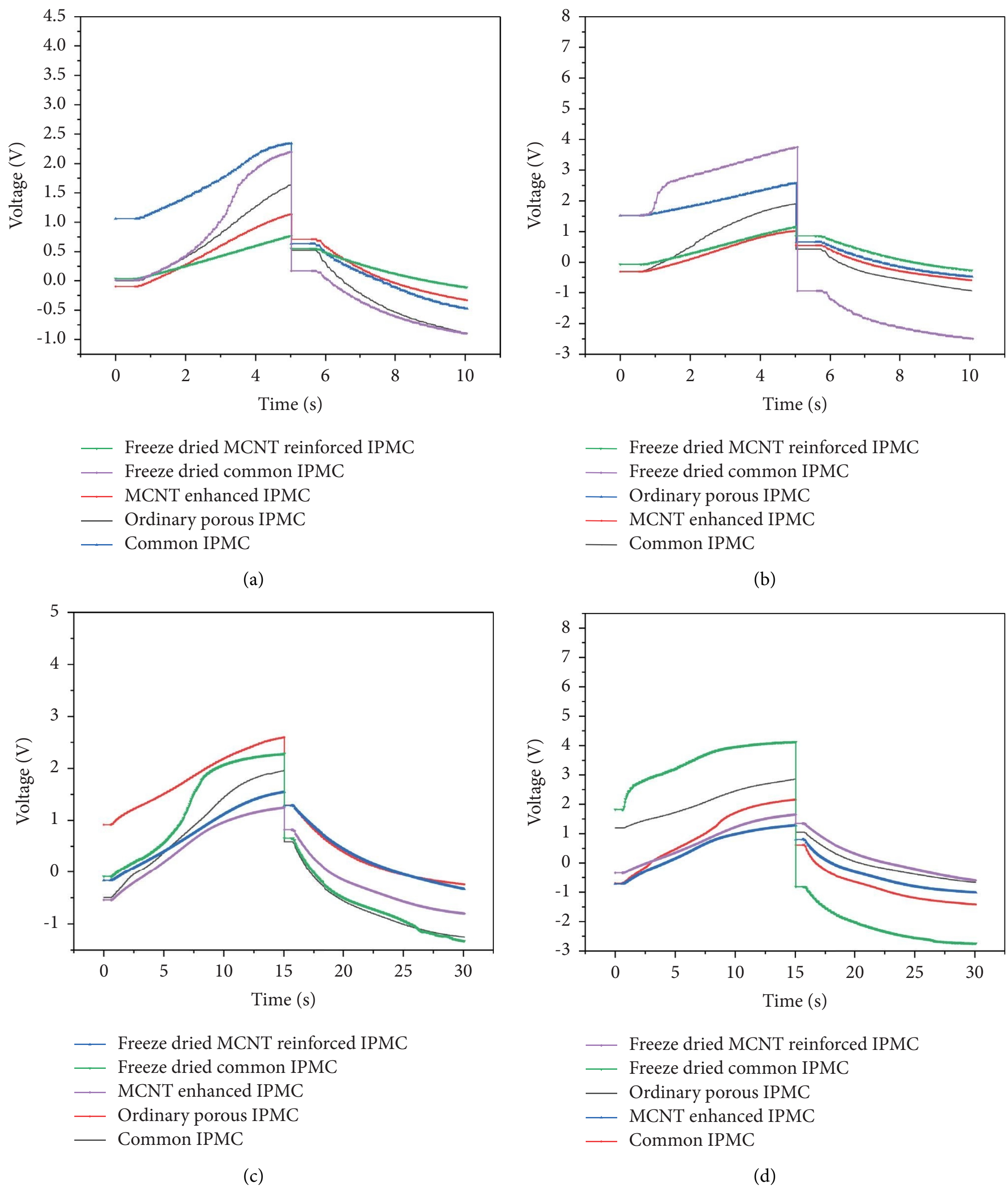


Figure 9: GCD curve of current in different sections: (a) 10 s interval, 1 mA; (b) 10 s interval, 1.5 mA; (c) 30 s interval, 1 mA; (d) 30 s interval, 1.5 mA.

on the surface was dried and weighed. Then, the IPMC was placed into a vacuum drying box and heated and evaporated at 120 degrees Celsius for 2 hours. The moisture content is shown in Figure 11.

As can be seen from Figure 11, the moisture content of porous IPMC is much higher than that of ordinary IPMC, and the moisture content of the IPMC prepared by freeze-drying is also much higher than that of the IPMC prepared by heat drying. The moisture content is almost the same as that of the porous film prepared by adding ZnO. However, due to the freezing mechanism of IPMC prepared by freeze drying, the pores in the film are more uniform. However, the common porous film with drying is not uniform due to zinc oxide precipitation, which can easily lead to internal stress in use and measurement. However, the preparation of IPMC by freeze drying alone will cause too much space in the ion exchange membrane, which will decrease the tensile capacity of the ion exchange membrane. In addition, repeated freeze drying is required to prepare an ion exchange membrane with suitable properties.

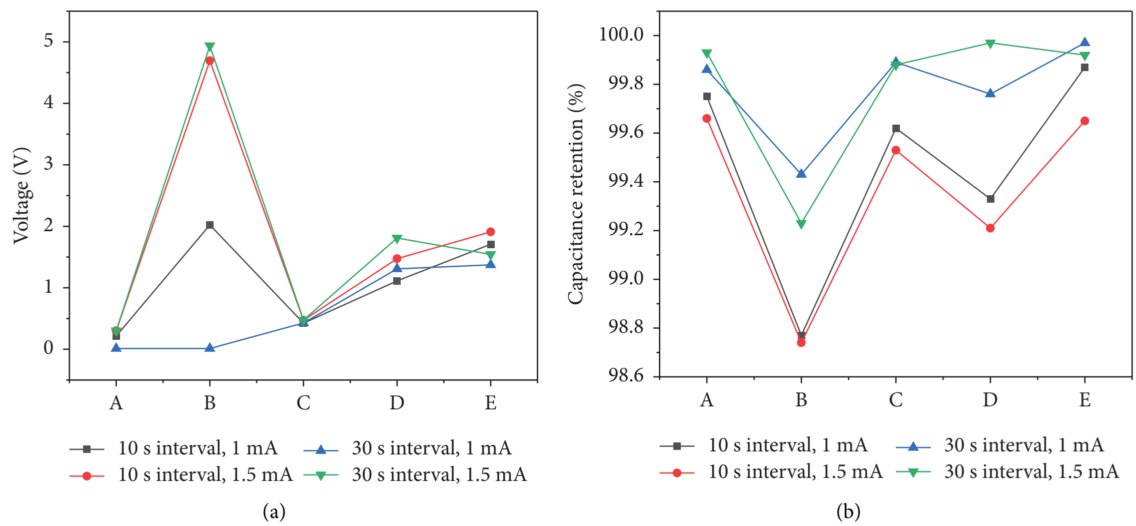


FIGURE 10: (a) Voltage drop; (b) capacitance retention. A: freeze-dried MWCNT-reinforced IPMC; B: freeze-dried common IPMC; C: MWCNT-enhanced IPMC; D: ordinary porous IPMC; E: common IPMC.

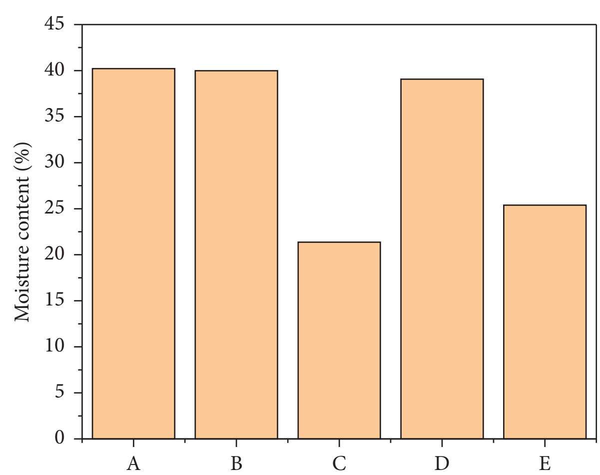


FIGURE 11: Moisture content: (a) freeze-dried MWCNT-reinforced IPMC; (b) freeze-dried common IPMC; (c) MWCNT-enhanced IPMC; (d) ordinary porous IPMC; (e) common IPMC.

## 4. Conclusion

In summary, a new method for the preparation of IPMC was designed and prepared in this study. In this method, the ion exchange membrane was doped with MWCNTs as reinforcement materials, and then, the ion exchange membrane was prepared by freeze-drying technology. The IPMC prepared has good electrical properties. The water content of the ion exchange membrane prepared by this technology can reach up to 40.21%. In this paper, the cyclic volt–ampere method is used for analysis. Under the scanning speed of 50 mV/s and the scanning interval of 2 V, the specific capacitance can reach 247.5335 $mF/cm^{-2}$, which is 24 times that of the IPMC prepared by the common method. At the same time, ac impedance analysis was used to calculate its ionic conductivity of 0.29391 mS/cm, much higher than that of other IPMCs. Higher ionic conductivity causes the IPMC to display better electrical performance, and also increases the IPMC's reaction rate in the process of electromechanical conversion and motor conversion. By doping MWCNTs in the ion exchange membrane, the problem wherein the toughness of the porous ion exchange membrane is poor and not easy to coarsen is solved. Meanwhile, the freeze-drying technology makes the MWCNTs and small cavities distributed in the ion exchange membrane more uniform. The internal stress of IPMC is reduced, and there is no need to add other toxic and flammable organic solvents to change the boiling point during the preparation process, making the preparation process safer.

The modification method described in this paper improved the electrochemical performance and the water content of IPMC, providing a new idea for the preparation of porous IPMC. At the same time, there was no need to add toxic solvents in the preparation process, which made the process safer and improved the lifetime of the IPMC. However, the IPMC preparation method described in this paper does not significantly improve its lifetime. In the future, further optimization of the IPMC preparation process is needed to prepare IPMCs with better performance and longer lifetimes, and IPMCs can thus be used in real-life applications as soon as possible.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

This study was supported by the Heilongjiang Provincial Natural Science Foundation of China (LH2020E089), Basic Scientific Research Program of Nantong City (JC22022014), Outstanding Young Core Teachers from the "Green-Blue Project" of Colleges and Universities in Jiangsu Province, China Postdoctoral Science Foundation (2021M691970), Postdoctoral Innovation Project of Shandong Province (202103051), and University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2018205).

## References

[1] X. Zhang, S. Yu, M. Li, M. Zhang, C. Zhang, and M. Wang, "Enhanced performance of IPMC actuator based on macroporous multilayer MCNTs/Nafion polymer," *Sensors and Actuators A: Physical*, vol. 339, no. 1, Article ID 113489, 2022.

[2] L. Calligaris, A. Cascadan, L. E. Ardila-Perez et al., "A flexible and low-cost open-source IPMC mezzanine for ATCA boards based on Open IPMC," *Journal of Instrumentation*, vol. 17, no. 3, Article ID c03007, 2022.

[3] L. Mohammad and M. Shaikh Hamid, "Anis Arfat et al., "A Convenient and Simple Ionic Polymer-Metal Composite (IPMC) Actuator Based on a Platinum-Coated Sulfonated Poly (ether ether ketone)-Polyaniline Composite Membrane," *Polymers*, vol. 14, no. 4, p. 50, 2022.

[4] T. Kikuchi, T. Takano, A. Yamaguchi, A. Ikeda, and I. Abe, "Haptic interface with twin-driven MR fluid actuator for teleoperation endoscopic surgery system," *Actuators*, vol. 10, no. 10, p. 245, 2021.

[5] T. Kikuchi, I. Abe, T. Nagata, A. Yamaguchi, and T. Takano, "Twin-driven actuator with multi-layered disc magneto-rheological fluid clutches for haptics," *Journal of Intelligent Material Systems and Structures*, vol. 32, no. 12, pp. 1326–1335, 2021.

[6] J. H. Lee, P. S. Chee, E. H. Lim, and C. H. Tan, "Artificial intelligence-assisted throat sensor using ionic polymer-metal composite (IPMC) material," *Polymers*, vol. 13, no. 18, p. 3041, 2021.

[7] Y. Xu, Ye. Du, X. Zhao, Y. Zhang, W. Jia, and X. Wen, "Research on Ag-IPMC force electric model and force output characteristics," *Ionics*, vol. 26, no. 8, pp. 4153–4162, 2020.

[8] Y. Xu, W. Jia, Y. Zhang, F. Wang, G. Zhao, and D. Zang, "Mechanical properties analysis and surface composition research of Ag-IPMC," *Sensors and Actuators A: Physical*, vol. 319, no. 3, Article ID 112565, 2021.

[9] L. Yang, D. Zhang, X. Zhang, A. Tian, and M. He, "Property of ionic polymer metal composite with different thicknesses based on solution casting technique," *International Journal of Modern Physics B*, vol. 34, no. 28, Article ID 2050263, 2020.

[10] R. Z. Ekbatani, Ke. Shao, J. Khawwaf et al., "Control of an IPMC soft actuator using adaptive full-order recursive terminal sliding mode," *Actuators*, vol. 10, no. 2, p. 33, 2021.

[11] W. jun Zhou, Y. xin Wu, H. q. Hu, Y. Li, and Y. Wang, "Port-Hamiltonian modeling and IDA-PBC control of an IPMC-actuated flexible beam," *Actuators*, vol. 10, no. 9, p. 236, 2021.

[12] E. Kociolek-Balawejder, E. Stanisławska, I. Jacukowicz-Sobala, and D. Ocinski, "CuO-loaded macroreticular anion exchange hybrid polymers obtained via tetrachlorocuprate(II) ionic form," *International Journal of Polymer Science*, vol. 2017, Article ID 4574397, 6 pages, 2017.

[13] H. Chen, M. Vahdati, P. Xiao, F. Dumur, and J. Lalevee, "Water-soluble visible light sensitive photoinitiating system based on charge transfer complexes for the 3D printing of hydrogels," *Polymers*, vol. 13, no. 18, p. 3195, 2021.

[14] L. N. Hao, Y. Chen, and Y. S. Zhao, "Research on enhanced performance of ionic polymer metal composite by multi-walled carbon nanotubes," *Materials Research Innovations*, vol. 19, pp. S1-S477–S1-481, 2015.

[15] Y. Wu, M. Yu, Q. He et al., "Axial motion characterization of a helical ionic polymer metal composite actuator and its application in 3-DOF micro-parallel platforms," *Actuators*, vol. 10, no. 10, p. 248, 2021.

[16] Z. Sun, W. Song, G. Zhao, and H. Wang, "Chitosan-based polymer gel paper actuators coated with multi-wall carbon nanotubes and $MnO_2$ composite electrode," *Cellulose*, vol. 24, no. 10, pp. 4383–4392, 2017.

[17] A. Madni, R. Kousar, N. Naeem, and F. Wahid, "Recent advancements in applications of chitosan-based biomaterials for skin tissue engineering," *Journal of Bioresources and Bioproducts*, vol. 6, no. 1, pp. 11–25, 2021.

[18] J. Li, A. Tian, X. Wang et al., "Dendrite growth and performance of self-healing composite electrode IPMC driven by $Cu^{+2}$," *ACS Omega*, vol. 7, no. 21, pp. 17575–17582, 2022.

[19] J. S. Swarrup, R. Ganguli, and G. Madras, "Analysis on enhancing the sensing behavior of ionic polymer metal composite based sensors," *Journal of Intelligent Material Systems and Structures*, vol. 32, no. 4, pp. 420–429, 2021.

[20] L. Yang, D. Zhang, X. Zhang, and A. Tian, "Electroless copper deposition and interface characteristics of ionic electroactive polymer," *Journal of Materials Research and Technology*, vol. 11, no. 36, pp. 849–856, 2021.

[21] J. Zhao, J. Shao, Z. Zhang, B. Liang, and X. Liu, "Preparation and characterization analysis of carbon nanotubes and graphene electrode modified carbon nanotubes reinforced IPMC," *Advances in Mechanical Engineering*, vol. 13, no. 8, p. 11, Article ID 168781402110407, 2021.

[22] Z. Sun, F. Li, D. Zhang, and W. Song, "High-performance all-gel-state nano-biopolymer artificial muscles enabled by macromolecularly interconnected conductive microporous chitosan and graphene loaded carbon nanosheet based ionic electrolyte membrane," *Journal of the Electrochemical Society*, vol. 165, no. 13, pp. H820–H830, 2018.

[23] A. Khan, R. K. Jain, P. Banerjee, Inamuddin, and A. M. Asiri, "Soft actuator based on Kraton with GO/Ag/Pani composite electrodes for robotic applications," *Materials Research Express*, vol. 4, no. 11, Article ID 115701, 2017.

[24] D. Wang, J. Nai, H. Li, L. Xu, and Y. Wang, "A robust strategy for the general synthesis of hierarchical carbons constructed by nanosheets and their application in high performance supercapacitor in ionic liquid electrolyte," *Carbon*, vol. 141, pp. 40–49, 2019.

[25] D. Wang, Z. Zhang, J. Sun, and Z. Lu, "From volatile ethanolamine to highly N, B dual doped carbon superstructures for advanced Zn-ion hybrid capacitors: unveiling the respective effects heteroatom functionalities," *Journal of the Electrochemical Society*, vol. 169, no. 7, Article ID 070511, 2022.

[26] D. Wang, Z. Pan, G. Chen, and Z. Lu, "Glycerol derived mesopore-enriched hierarchically carbon nanosheets as the cathode for ultrafast zinc ion hybrid supercapacitor applications," *Electrochimica Acta*, vol. 379, no. 1, Article ID 138170, 2021.

[27] H. F. Pinto, A. G. B. da Cruz, S. Ranjbarzadeh, and F. P. Duda, "Predicting simulation of flow induced by IPMC oscillation in fluid environment," *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, vol. 40, no. 4, p. 203, 2018.

[28] Z. Sun, S. Du, F. Li, L. Yang, D. Zhang, and W. Song, "High-performance cellulose based nanocomposite soft actuators with porous high-conductivity electrode doped by graphene-coated carbon nanosheet," *Cellulose*, vol. 25, no. 10, pp. 5807–5819, 2018.

[29] B. De, S. Banerjee, V. Kapil Dev, P. Tanvi, P. K. Manna, and K. K. Kamal, "Carbon nanotube as electrode materials for supercapacitors," *Chemical Industry Times*, vol. 302, no. 1, pp. 229–243, 2020.

[30] R. A. Brazhe and A. F. Savin, "Capacitance sensors based on nanotube supercondensers," *Russian MicroElectronics*, vol. 46, no. 7, pp. 506–509, 2017.

[31] E. Mark, "Orazem, Bernard Tribollet, "A tutorial on electrochemical impedance spectroscopy," *ChemTexts: The Textbook Journal of Chemistry*, vol. 6, no. 3, p. 12, 2020.

[32] M. Samadpour, M. Dehghani, P. Parand, M. Natagh Najafi, and E. Parvazian, "Photovoltaic performance and electrochemical impedance spectroscopy analysis of CdS/CdSe-sensitized solar cell based on surfactant-modified ZnS treatment," *Applied Physics A*, vol. 126, no. 6, p. 461, 2020.