

Electrochromic iontronic devices based on nanoscale cell membrane-inspired hydrated ion channels in Nafion solid polyelectrolyte

BO LI^{1(a)}, JINGE MA¹, YANJIE WANG², HUAJING FANG³ and GUIMIN CHEN¹

¹ Shaanxi Key Laboratory for Intelligent Robots, School of Mechanical Engineering, Xi'an Jiaotong University - Xi'an, 710049, China

² Jiangsu Key Laboratory for Special Robot Technology, School of Mechanical and Electrical Engineering, Hohai University - Changzhou Campus, Changzhou, 213022, China

³ State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi'an Jiaotong University - Xi'an, 710049, China

received 10 September 2019; accepted in final form 20 December 2019

published online 4 February 2020

PACS 82.47.Tp – Electrochemical displays

PACS 88.30.mg – Inorganic proton conductors

PACS 85.50.-n – Dielectric, ferroelectric, and piezoelectric devices

Abstract – An ion channel in a cell membrane offers a path of ion migration for perception and communication in biology. Under this inspiration, in this paper, the hydrated ion channel is introduced in a solid Nafion polyelectrolyte for electrochromic (EC) iontronic device based on WO₃. The hydrated ion channels can effectively regulate the coloration when gating the ion migration and injection into the WO₃. The coloration is characterized at different voltages in time responses. A transmission change over 50% at 400 nm is realized. This offers a new route to design functional EC iontronics that encoded the bio-mechanism.

Copyright © EPLA, 2020

An electrochromic (EC) device is an important device that can change its color under an applied electric potential. The EC device has been widely exploited in optical applications, including the smart window, the flexible screen, and efficient displays, etc. [1–6]. Among these EC techniques, the one which uses WO₃ as an essential coloration material has been much studied, owing to its advances in low cost, easy fabrication and good stability [7,8]. The color change of WO₃ is the result of dual injection/extraction by electrons and cations, respectively. In the coloration process, under an electric field on the EC device, the cations and electrons are injected into WO₃, which changes its color from transparent to deep blue. In the bleaching process, under a reverse electric field, the cations and electrons are extracted, consequently, the color in WO₃ is bleached [9].

In a WO₃-based EC device, the source of electrons is provided by a transparent electrode, *i.e.*, either ITO or FTO. The cations are provided by a different electrolyte material, including the liquid, the solid hydrogel

and the rigid solid film. In the literature we find that the polymer electrolyte offers good properties: easy processing, mechanical strength, enhanced endurance and robustness [8,10–19]. Therefore, in this paper, we fabricate a new type of EC iontronic device utilizing another polymer electrolyte with hydrate ion channel to regulate the coloration, which is inspired by the ion migration in a cell membrane. We show the bio-inspired concept, investigate the experimental technique to fabricate the layered polyelectrolyte and characterize the coloration process.

Figure 1 shows the bio-inspiration concept. In a cell, the membrane potential can be generated by ion transport through the phospholipid bilayer, known as the ion channel in fig. 1(a). The cell membrane potential offers perception for tactile and auditory sensing [20,21]. We incorporate this functional ion channel into the polyelectrolyte during the design of the EC device in fig. 1(b), adding the bio-feature to regulate the coloration. Subject to a voltage <5 V, the protons, H⁺, migrate in the channel through the interface, then exchange with the protons in WO₃. Meanwhile, the electrons are injected into WO₃ as well. Figure 1(c) sketches the process in the chemical

^(a) E-mail: liboxjtu@mail.xjtu.edu.cn (corresponding author)

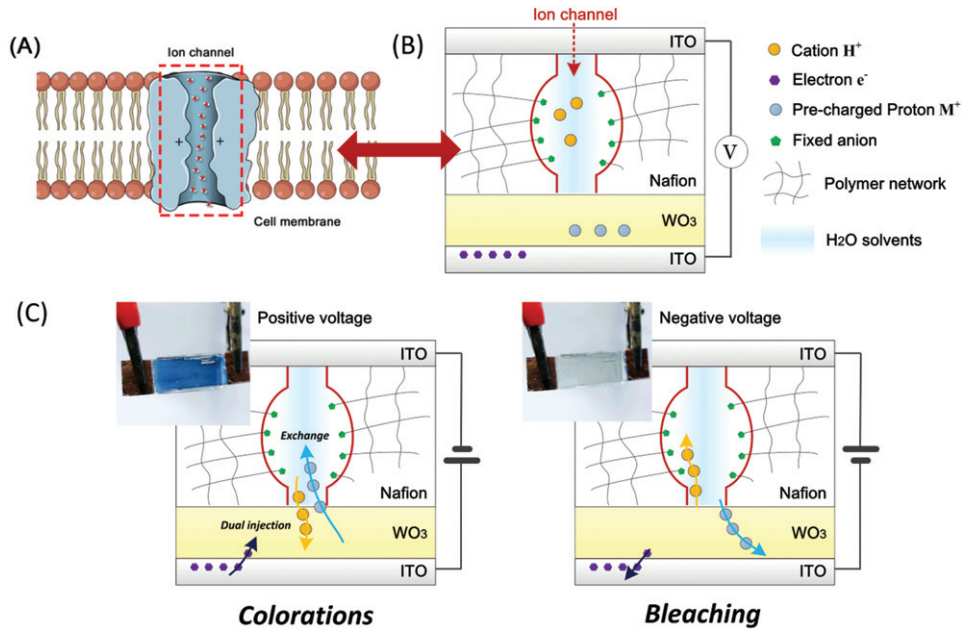


Fig. 1: The bio-inspired design and concept of electrochromic (EC) iontronics. (a) The ion channel in a cell membrane. (b) The hydrate ion channel in the polyelectrolyte of an EC device. (c) The coloration and bleaching reaction in WO_3 during the dual-injection process.

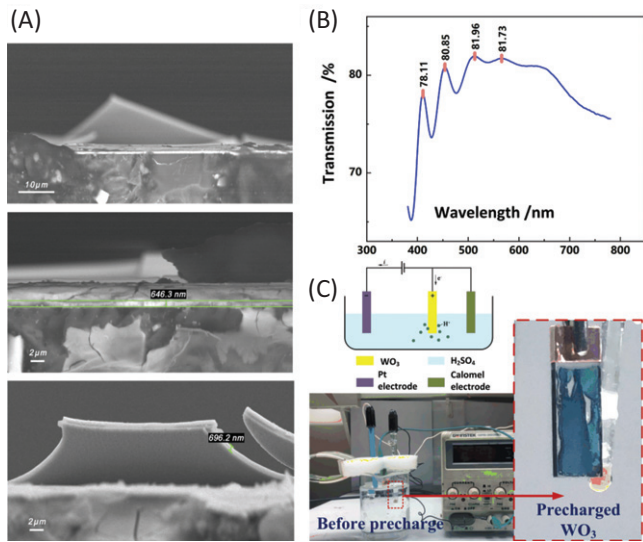


Fig. 2: Characterization of the WO_3 film. (a) The SEM image of the double layered WO_3 film (666.2 nm thickness). (b) The transmission of the film. (c) The pre-charged WO_3 film which verifies its capability of electrochemical coloration.

reaction. Apparently, the ion channel provides a path for effective ion migration for regulation and gating the chemical reaction.

The synthesis of WO_3 is provided in the materials and method section. In fig. 2(a), SEM images characterize the two-layered WO_3 film with thickness of 666.2 nm. Figure 2(b) is the transmission of the WO_3 film at the original state. In fig. 2(c), by pre-charging the WO_3 film in a reservoir, the protons are installed in WO_3 . This process verifies the coloration capability of WO_3 .

We use the Nafion film from Dupont Company as the perfluorosulfonate polyelectrolyte. Nafion is a commercial product known for its outstanding performance in ion-exchange, and it has been used in fuel cells for ion storage [22]. Owing to the cluster surrounded by fixed anions, hydrate ion channels are naturally formed during the synthesis for the motion of cations in the water environment [23]. A Nafion film has been employed in the study of fuel cell batteries for its outstanding stability compared to Li ion ones [11], as well as in the artificial muscle for a biomimetic robot owing to the ion transportation [24–26]. Here, we employ the Nafion film to utilize its ion transport in the nanochannel for EC coloration. In order to provide a sufficient amount of cation for coloration, two types of Nafion are available: a multi-layered membrane laminate and a Nafion block, which are sketched in fig. 3(a). Due to the contrast of the width of ion channel (10^{-10} m) and the length of EC iontronics (10^{-2} m), in a commercially available Nafion film (117 series) whose thickness is 180 μm , the ion channels are non-directionally distributed, but form a 3D path, thus the ion migration is not effectively delivered to reach the interface [23,27,28]. However, by stacking ultra-thin layered Nafion films ($<1 \mu\text{m}$), the ion channels are in parallel arranged and connected through the overall membrane thickness. Therefore, we recasted and stacked the ultra-thin Nafion polyelectrolyte on a well deposited WO_3 film.

To improve the cation concentration, the Nafion solution was condensed by mixing with a dimethylethylenediamine solution in a volume ratio of 4:1. The mixed solution was heated at a temperature of 70 $^{\circ}\text{C}$ and stirred at a rotation speed of 800 rpm for condensing. The volume

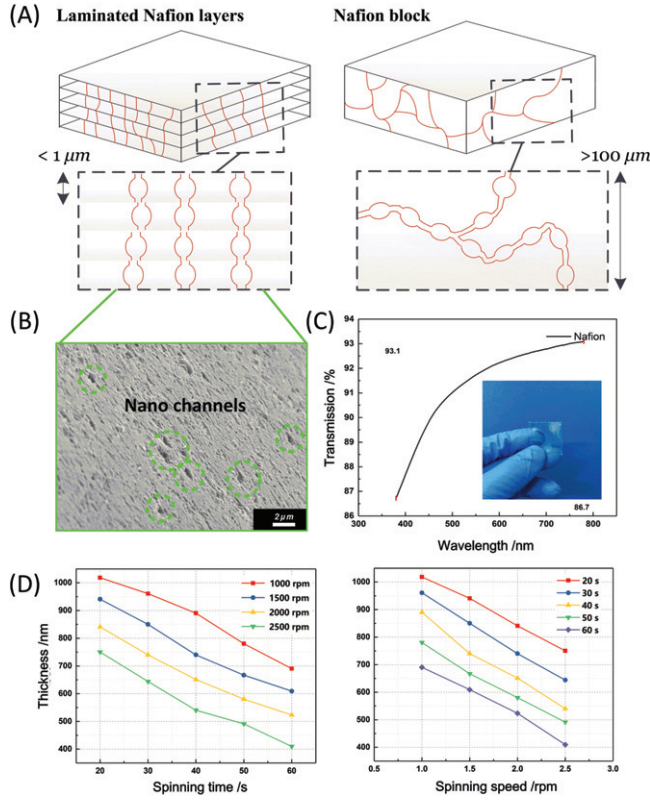


Fig. 3: The ion channel path and fabrication of Nafion-based polyelectrolytes. (a) Comparison of layered thin-Nafion films and a Nafion block in ion channel distribution. (b) The condensed Nafion solution. (c) The optical transmission of ultra-thin Nafion as a fully transparent polyelectrolyte. (d) The thickness of the ultra-thin polyelectrolyte under different spin-coating speed and time.

of the Nafion content after concentration is calculated by $C_{condense} = \frac{V_{original} \times 5\%}{V_{condense}}$, where $C_{condense}$ is the concentration of the condensed liquid, $V_{original}$ is the volume of the original Nafion solution, $V_{condense}$ is the condensed volume, 5% is the concentration of the original Nafion solution. The experimental design for condensation is listed in table S1 of the Supplementary Material [Supplementarymaterial.pdf](#) (SM). The surface of the Nafion membrane is characterized in fig. 3(b) to show the channel size. When the concentration of the condensed solution is greater than 20%, the agglomeration phenomenon occurs during the concentration process and fails to form a homogenous solution, which is also verified by a similar report [29]. Therefore, we select the concentration of 20% in the spin-coating process for recasting the ultra-thin film.

Then the solution was spin-coated for recasting. Figures 3(c) and (d) show the coating results. Each film was heated at 80°C for 10 min. The spinning time and speed affect the thickness of the Nafion film concurrently. An ultra-thin Nafion film can be obtained at thickness between 400 and 1000 nm. In fig. 3(c), 8 layers of Nafion films, 1000 nm for each layer, were fabricated, which are fully transparent in the visible range, with a transmission up to 93.1%.

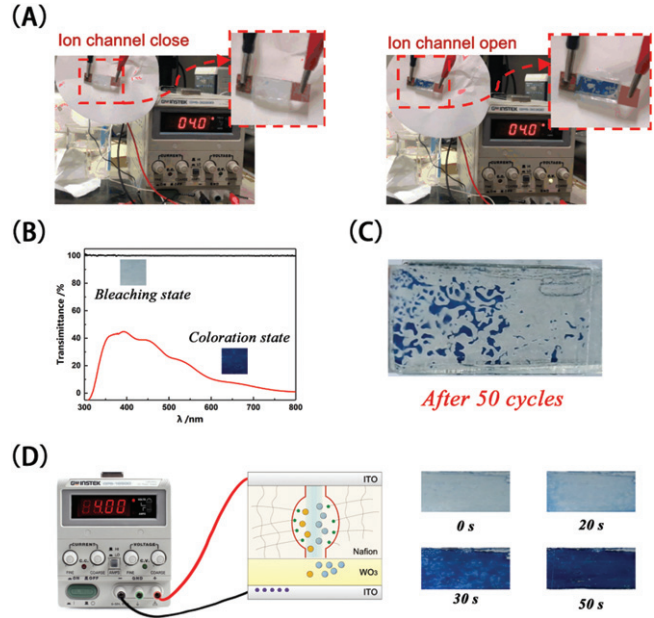


Fig. 4: Effect of the hydrate ion channel gating on the coloration. (A) The corresponding coloration on and off. (B) Characterization of the coloration. (C) The color stains due to the residual cation in the WO₃ film as the ion channel is closed. (D) The coloration of EC iontronics in time response.

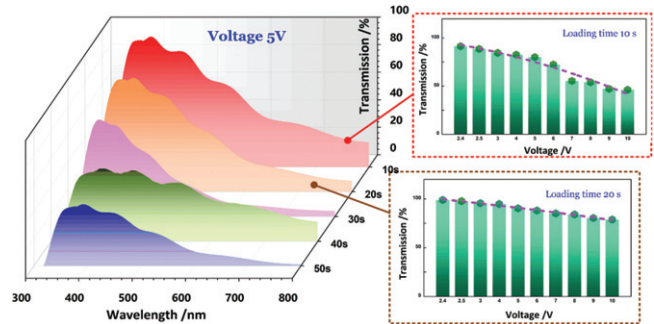


Fig. 5: The coloration at two loading times under 5 V.

In fig. 4(a), two EC iontronic devices were fabricated with a 8-layer coated Nafion film as polyelectrolyte layer on WO₃ and covered with ITO on both surfaces. The thickness for the WO₃ and polyelectrolyte is 333 nm and $8 \mu\text{m}$. When the polyelectrolyte layer was completely dry during the heating, the ion channel was closed and the ions hardly migrated without water to exchange with protons in WO₃, and the coloration was not triggered. With water absorbed, the polyelectrolyte layer swelled, opening its ion channels, and consequently the coloration was realized. The EC iontronic devices change their color under 4 V voltage, showing a difference in transmission over 53.85% in fig. 4(b). The coloration can be bleached by reversing the electric field. Through a repeated coloration and bleaching cycle of 50 times, some color stains appear within WO₃ in fig. 4(c). This is due to the loss of water in dry in the air as well. The ion channel is closed and

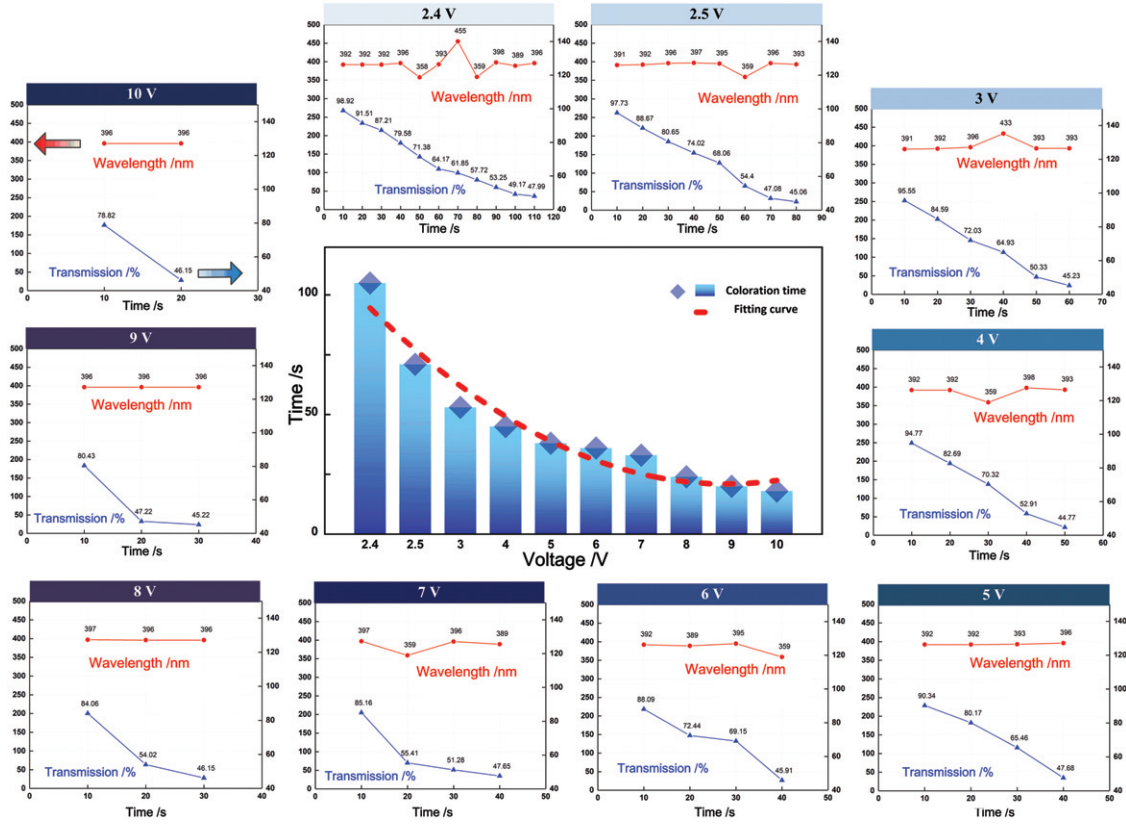


Fig. 6: The coloration in the EC iontronics. Small surrounding panels: the characterization of the maximum transmission value and wavelength in the coloration at different voltage. Big central panel: the maximum loading time for reaching a final color state.

hinders the cation to return to the polyelectrolyte, and as a consequence, the coloration stays. The stains of color are fully erasable by water absorption. Figure 4(d) displays the coloration process in time response.

After verifying that the ion channel can regulate the coloration, in fig. 5, the process of coloration under a constant voltage 5 V was characterized for an example. In fig. 5, the light transmissions of the EC iontronics were measured at different time intervals (10 s, 20 s, 30 s, 40 s, 50 s), showing the process of coloration with a peak value at a wavelength of 400 nm. In the two subplots of fig. 5, two time intervals were selected at 10 s and 20 s respectively, where the peak transmissions were recorded with regards to the increasing voltage. It is significant that a higher voltage promotes the coloration in the time domain, and all the EC iontronics reached a stable state gradually. Here we define the transmission of 47% as the final coloration state.

In fig. 6 (big central panel, top), under each voltage, the peak value of transmission and the corresponding wavelength were measured to characterize the coloration performance. Surely, a higher voltage accelerates the migration of a cation through the polyelectrolyte film and its insertion into the WO_3 quickly. We use the transmission at the final coloration state as a stop time T_c for characterizing the color efficiency, and the values are

summarized in table S2 of the SM as well as in fig. 6 (big central panel, bottom). Through the curve fitting, the effective coloration voltage can be expressed as $U = 114.48 - 21T_c + 1.19T_c^2$. This offers a control strategy for coloration.

The EC device features a fast coloration owing to the electrochemical reaction. An improvement has been made in either the electrode for functional and transparent conduction, or the electrolyte for proton storage. In this paper, Nafion is selected to provide a new media for hosting ion migration. Through the hydrated path of nano channels in Nafion, the movement of the ions is regulated for fast delivery to the interface of Nafion and WO_3 . Due to the robustness of Nafion, this electrolyte has been widely exploited in the application of fuel battery for stable lithium storage. For the EC device, the advantage of Nafion is that it contributes to the stability of the coloration, which may extend the time duration of the open-circuit memory effect.

In summary, inspired by the functional ion channel in the cell membrane, an electrochromic (EC) iontronic device is designed and fabricated, by laminating ITO/ WO_3 . A polyelectrolyte, Nafion, is re-casted to form a nanoscale hydrate ion channel. By stacking the thin layers of polyelectrolyte films, the ion channels are connected and oriented in a path, instead of forming a 3D complex map.

The ion channel turns the coloration on/off by regulating the ion migration through the interface, or their stay within the WO₃ layer as a coloration memory effect. A significant coloration is realized at different voltage levels. The effective coloration is characterized and analyzed, for guidance of bio-inspired iontronics in optical applications.

* * *

The authors acknowledge NSFC (Grant No. 91748124) and National Defense Science and Technology Bureau Basic Research Project for the financial support. Special thanks to Dr. DONGXU ZHAO for the experiments on the nanochannels in Nafion.

REFERENCES

- [1] ROWLEY N. M. and MORTIMER R. J., *Sci. Prog.*, **85** (2002) 243.
- [2] WANG Y. *et al.*, *Annu. Rev. Chem. Biomol. Eng.*, **7** (2016) 283.
- [3] CAI G. *et al.*, *Adv. Sustain. Syst.*, **1** (2017) 1700074.
- [4] CHUA M. H. *et al.*, *Introduction to electrochromism*, in *Electrochromic Smart Materials* (The Royal Society of Chemistry) 2018, p. 1, DOI: 10.1039/9781788016667-00001.
- [5] GRANQVIST C. G. *et al.*, *Electrochim. Acta*, **259** (2018) 1170.
- [6] LI N. *et al.*, *Small*, **15** (2019) e1804974.
- [7] ARVIZU M. A. *et al.*, *Thin Solid Films*, **653** (2018) 1.
- [8] ZHAO Q. *et al.*, *Sol. Energy Mater. Sol. Cells*, **194** (2019) 95.
- [9] FANG H. *et al.*, *Mater. Horiz.*, **5** (2018) 1000.
- [10] THAKUR V. K. *et al.*, *Adv. Mater.*, **24** (2012) 4071.
- [11] ZHANG H. and SHEN P. K., *Chem. Rev.*, **112** (2012) 2780.
- [12] COSSARI P. *et al.*, *Solid State Ion.*, **317** (2018) 46.
- [13] DONG D. *et al.*, *Appl. Surf. Sci.*, **357** (2015) 799.
- [14] QU H. *et al.*, *Sol. Energy Mater. Sol. Cells*, **163** (2017) 23.
- [15] WANG Y. *et al.*, *Nat. Mater.*, **18** (2019) 1335.
- [16] XIONG S. *et al.*, *J. Macromol. Sci. Part B*, **54** (2015) 799.
- [17] ZHANG K. *et al.*, *J. Mater. Sci.: Mater. Electron.*, **29** (2018) 14803.
- [18] ZHANG W. *et al.*, *Nat. Commun.*, **10** (2019) 1559.
- [19] DONG D. *et al.*, *Appl. Surf. Sci.*, **383** (2016) 49.
- [20] YUK H. *et al.*, *Chem. Soc. Rev.*, **48** (2019) 1642.
- [21] CHEN W. *et al.*, *J. Mater. Chem. C*, **7** (2019) 3744.
- [22] PEIGHAMBARDoust S. J. *et al.*, *Int. J. Hydrog. Energy*, **35** (2010) 9349.
- [23] MAURITZ K. A. and MOORE R. B., *Chem. Rev.*, **104** (2004) 4535.
- [24] CHEN Z., *Robot. Biomim.*, **4** (2017) 24.
- [25] SHAHINPOOR M., *Electrochim. Acta*, **48** (2003) 2343.
- [26] BHANDARI B. *et al.*, *Int. J. Precis. Eng. Manuf.*, **13** (2012) 141.
- [27] SCHMIDT-ROHR K. and CHEN Q., *Nat. Mater.*, **7** (2008) 75.
- [28] HSU W. Y. and GIERKE T. D., *J. Membr. Sci.*, **13** (1983) 307.
- [29] COSSARI P. *et al.*, *Sol. Energy Mater. Sol. Cells*, **155** (2016) 411.