A mesoporous SiO$_2$ thin films-based ionic decision-maker for solving multi-armed bandit problems

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An ionic decision-maker (IDM), with the remarkable ability to solve multi-armed bandit problems (MBPs), has been developed as a new artificial intelligence technology, which have humanlike decision-making capabilities. Owing to their low durability, the Nafion polymer electrolytes and electrode materials normally found within IDMs do not meet the high-level integration and repetitive operation requirements of such devices. Therefore, in this study, mesoporous SiO$_2$, which is a proton conducting inorganic oxide, has been utilized as the IDM electrolyte. The oxide-based IDMs developed showed good solvability for MBPs and excellent adaptability to dramatic environmental shifts, which were both at similar levels to those found in Nafion-based IDMs. While the adaptation exhibited by the oxide-based IDMs was slightly inferior to that found in Nafion-based IDMs, fluctuations in the correct selection rate (CSR) were significantly improved over those observed in Nafion-based IDMs. Further, the average of reached CSR was enhanced to 0.96 in comparison to 0.92 for Nafion-based IDMs.© 2020 The Japan Society of Applied Physics

1. Introduction

Decision-making, one of the intellectual abilities possessed by living organisms, enables said organisms to adapt to and survive in dramatically changing environments. The realization of more sophisticated decision-making abilities may lead to higher-standards of life by maximizing the profit of whole societies since such abilities can be applied to various fields (e.g. cognitive radio, web advertising, financial trading, and the game of GO). Due to their user-friendliness, conventional computer science and technologies composed of a central processing unit (CPU), memory, and software programming, have attracted particular attention for their use in the development of artificial intelligence (AI) with decision-making abilities. However, computer-based AI will not be able to handle the currently enormous and exponentially increasing amount of information because the development of conventional electronics devices is reaching its limit.

Recent years have seen the active development of nanoionic devices, which have unique properties that differ from those found in electronics devices due to carrier modulation induced by ion transport. One particular example of such a nanoionic device is the ionic decision-maker (IDM), which was developed as a new AI technology with decision-making abilities. IDMs are based on nanoionic phenomena within proton conducting polymer electrolytes. These devices have the ability to make decisions, without CPU-based computation, by referring to past experience as the concentration modulation of ions and molecules. Moreover, IDM-based computing systems consume less power than CPU-based computing systems and have demonstrated excellent solvability of multi-armed bandit problems (MBPs), which are fundamental mathematical problems applicable to deep learning and related technologies. They also exhibit remarkable adaptability to sudden environmental changes. The solving properties of MBPs are comparable to those found in conventional CPU-based computation (e.g. greedy and softmax).

For applications, it is necessary to maintain the repetitive operations of highly-integrated IDMs so as to solve more complex MBPs. However, the Nafion and Pt/C catalyst layers within the IDMs have proved to be unsuitable for integrated device fabrication and repetitive pulse current applications due to their low durability. In this study, instead of using Nafion as the IDM electrolyte, we turned our attention to proton conducting inorganic oxides, which have excellent durability and compatibility with conventional semiconductor technologies. Although at room temperature the proton conductivity of inorganic oxides is usually much lower than that of Nafion (approx. $10^{-2} \text{S cm}^{-1}$), mesoporous SiO$_2$ has relative high proton conductivity above $10^{-4} \text{S cm}^{-1}$; possibly high enough for IDM operations. Therefore, the aims of this work are the development and evaluation of oxide-based IDMs. Here, we show that the solving properties of the said oxide-based IDMs, derived from the chemical stability of SiO$_2$, are superior to those of Nafion-based IDMs.

2. Experimental methods and theoretical background

2.1. Fabrication and evaluation of mesoporous SiO$_2$ thin films

250 nm thick mesoporous SiO$_2$ thin films were deposited by the sol-gel method and spin-coating. Si(OCH$_3$)$_4$ (TEOS, 95%), CH$_3$(CH$_2$)$_3$N$^+$(CH$_3$)$_2$Br$^-$ (CTAB, 98%), 1-C$_3$H$_7$OH (99.5%), and (C$_2$H$_5$O)$_3$PO (97%) were obtained from Wako. At first, 2.2 g of CTAB was dissolved in 30 ml of 1-C$_3$H$_7$OH at 90 °C. Secondly, 10 ml of TEOS was hydrolyzed at 60 °C with a solution composed of 3.5 ml of 1-C$_3$H$_7$OH, 4.0 ml of 0.02 M HNO$_3$, and 4.0 ml of distilled H$_2$O. After hydrolyzing, CTAB dissolved in 30 ml of 1-C$_3$H$_7$OH and 0.4 ml of (C$_2$H$_5$O)$_3$PO were added to the hydrolyzed TEOS solution. The precursor solution was coated onto SiO$_2$ glass substrates by spin-coating at 2000 rpm for 30 s. The spin-coated samples were aged at room temperature, in ambient atmosphere, for 48 h so as to evaporate the solvent and gain the ordered CTAB. Finally, mesoporous SiO$_2$ thin films were obtained by heating the samples at 400 °C in air for 5 h in order to remove CTAB.

Two 2 mm × 2 mm square electrodes, consisting of 5 nm thick Ti and 100 nm thick Pt thin films, were deposited by RF magnetron sputtering with a shadow mask on the surface of...
the mesoporous SiO$_2$ thin films. Ti thin films were used as buffer layers. The distance between the electrodes was 100 $\mu$m.

The mesoporous structure of the prepared SiO$_2$ thin films was investigated by out-of-plane X-ray diffraction (XRD) with Cu K$_\alpha$ using SmartLab (Rigaku).

The total conductivity of a Pt/mesoporous SiO$_2$/Pt cell was characterized by AC impedance spectroscopy with a constant voltage of 0.1 V, at frequencies ranging from 0.01 Hz to 1 MHz at various temperatures and relative humidities (RH). RH was controlled by introducing dry N$_2$ gas and H$_2$O bubbled at different temperatures.

### 2.2. Multi-armed bandit problems

Many problems that AI with decision-making functions should solve under various situations are interpreted as MBPs, which are mathematical problems related to strategies that require a gambler to select the optimal slot machine (SM) so as to maximize the total rewards in a series of trials, as shown in Fig. 1. In these problems, the gambler can select one of multiple SMs at a certain time $t$. For example, suppose that a gambler selects either SM A or B, which gives rewards (coins) with reward probabilities $P_A$ and $P_B$ and no rewards (no coins) with probabilities $1 - P_A$ and $1 - P_B$, respectively. At first selection, the gambler does not know the value of $P_A$ and $P_B$. The gambler should, as quickly and accurately as possible, find the SM with the highest probability based on his past experiences of playing the SMs.

### 2.3. Setting and operation of oxide-based IDMs

Figure 2 is an illustration of a computing system that is using oxide-based IDMs to select either SM A or B, which gives rewards (coins) with reward probabilities $P_A$ and $P_B$ and no rewards (no coins) with probabilities $1 - P_A$ and $1 - P_B$, respectively.

This sequence of steps is defined as one selection, which was repeated. Figure 3 shows the variation in voltage between the electrodes during the operation of the IDMs. The results of playing the SMs up to the 6th selection are shown in Table I. At the first selection, the oxide-based IDMs selected SM B because the voltage was negative. A pulse current of 10 nA was then applied to the electrodes for 500 ms in accordance with the result, obtained by a random number, that the selected SM B gave no rewards. After opening of the circuit for 500 ms, SM A was selected owing to the positive voltage obtained at the second selection. A pulse current of −10 nA was then applied because the selected SM A did not give a reward. Such voltage modulation, based on proton migration in the electrolytes, was performed by employing charge-conserving TOW dynamics.

### 3. Results and discussions

#### 3.1. Structural and electrical characteristics of mesoporous SiO$_2$ thin films

The out-of-plane XRD pattern of the prepared mesoporous SiO$_2$ thin films is shown in Fig. 4. This pattern, at 2θ values of 4.84°, is estimated to be a two-dimensional hexagonal mesoporous structure (p6mm) with $d$(100) of 1.83 nm. The absence of (110) reflection, which is a typical XRD pattern for a hexagonal structure, was attributed to the orientation of the hexagonal unit cell with the $c$ and $a$ axes parallel to the substrates.

Figure 5 shows the AC impedance spectrum of the Pt/mesoporous SiO$_2$/Pt cell, measured at 25°C and RH 70%. The semicircles in the higher frequency range and the lower frequency range are attributed to ionic conduction in the mesoporous SiO$_2$ thin films and at the mesoporous SiO$_2$ thin film/electrode interfaces, respectively. By using the diameter of the semicircle in the higher frequency region as the in-plane resistance, the ion conductivity of the mesoporous SiO$_2$ thin films calculated was to be $1.29 \times 10^{-8}$ S cm$^{-1}$, which is a typical proton conductivity for mesoporous SiO$_2$ thin films at room temperature. Figure 6 shows the total electrical conductivity of the mesoporous SiO$_2$ thin films, measured at 25°C and various RH. The conductivity was enhanced with increasing RH. Moreover, this value drastically decreased below RH 40%. Figure 7 shows the Arrhenius plots of the total electrical conductivity of the mesoporous SiO$_2$ thin films at a fixed water vapor pressure of 3.17 $\times$ 10$^4$ Pa, which is the saturated water pressure at 25°C. The water vapor pressure was maintained by passing N$_2$ gas through a bubbler with water at 25°C and supplying it to the sample chamber. The conductivity showed a significant decrease as temperature was varied from to 30°C to 100°C. It is quite reasonable.
because proton conductivity of mesoporous SiO$_2$ is positively correlated with RH due to the effect on H$_2$O molecules absorption in mesopore structure, as seen in Fig. 6.\textsuperscript{25-33} In the present temperature range, RH steeply decreases with temperature (e.g. Given the fixed water vapor pressure of
prepared mesoporous SiO\(_2\) thin films. Figure 8 shows the solving properties, achieved by the oxide-based IDMs had no information about these SMs and randomly selected one of them. As the oxide-based IDMs repeatedly selected a SM, the CSR rapidly increased toward 1. This increment indicates that the IDMs preferentially selected the optimal SM A based on past experience. Moreover, the CSR decreased to 0 immediately after revision of the reward probability, and again swiftly increased toward 1. These results clearly demonstrate that the oxide-based IDMs are able to solve the MBP and to adapt to environmental changes. This behavior corresponds to the voltage modulation caused by the electrical double layer charging and the redox reaction of protons, as shown in Eqs. (2) and (3).

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2, \quad (2) \]

\[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2e^- + 1/2\text{O}_2. \quad (3) \]

The solving properties, which are similar to those achieved by the Nafion-based IDMs, indicated that the proton conductivity of mesoporous SiO\(_2\) thin films was high enough to be utilized as the IDM electrolytes. However, there were some small differences in the solving properties of the two IDMs. Whereas the adaptation of the oxide-based IDMs was slightly slower than that of the Nafion-based IDMs, the fluctuation in CSR, which was significant in the Nafion-based IDMs, was much reduced in the oxide-based IDMs. Furthermore, the average reached CSR of 0.96, after every 200 selections, achieved by the oxide-based IDM is higher than the CSR of 0.92 achieved by the Nafion-based IDMs.

One possible reason for this disparity is a difference in chemical stability for repetitive pulse current applications. Various degradation mechanisms have been reported for proton-exchange membrane cells composed of a Nafion matrix and Pt/C catalyst layers.\(^{19-24}\) For instance, the H\(_2\)O\(_2\) induced degradation mechanism proposes the loss of sulfonic acid, which plays a major role in the proton conductivity of Nafion, because H\(_2\)O\(_2\), which is generated by oxygen reduction at the electrolyte/electrode interfaces, decomposes the main-chain and the side-chains of the Nafion matrix.\(^{19,20}\) The main effect of this degradation may be degradation of the Nafion-based IDM computing performance as the pulse currents are repeatedly applied. In contrast, the mesoporous SiO\(_2\) matrix, which is formed by strong Si–O bonding, had sufficient durability for the yielded H\(_2\)O\(_2\)\(^{43}\). Therefore, oxide-based IDMs may show smaller fluctuations in CSR and a higher average of reached CSR compared to Nafion-based IDMs. Furthermore, C-supported catalyst corrosion causes a decrease of the electrode surface area.\(^{23,24}\) In this mechanism, Pt nanoparticles separate from the electrodes because carbon atoms are converted to CO\(_2\) by reacting with H\(_2\)O. Therefore, it is advantageous for the oxide-based IDMs not to need C-supported catalysts.

\[ \text{CSR} = \frac{N}{C}. \quad (1) \]

Here, \(N\) is the number of cycles in which the optimal SM was selected for each selection, and \(C\) is the total number of cycles (\(C = 100\)).

### 3.2. Oxide-based IDM computing performance for MBPs

Figure 8 shows the solving properties, achieved by the oxide-based IDMs and Nafion-based IDMs, of a MBP for one gambler and two SMs.\(^{14}\) In the first 200 selections, \(P_A (=0.6)\) is higher than \(P_B (=0.4)\). After the 200th selection, \(P_A\) and \(P_B\) were reversed so as to emulate environmental changes (\(P_A = 0.4, P_B = 0.6\)). The total of 800 selections was defined as 1 cycle. A total of 100 cycles was performed during operation of the IDMs. Correct selection, which means IDMs select the optimal SM with the highest reward probability regardless of whether the IDMs are rewarded or unrewarded from the selected SM, is defined in order to evaluate solvability. Therefore, the correct selection rate (CSR), which represents the rate at which the IDMs select the optimal SM for each selection, is determined by Eq. (1).
In this study, proton conducting mesoporous SiO\(_2\) thin films were applied to IDM electrolytes to achieve highly-integrated device fabrication and repetitive operations. Excellent MBP solving properties and adaptation to environmental shifts were achieved by the operation of the mesoporous SiO\(_2\)-based IDMs, which are in turn compatible with conventional semiconductor technologies. Their computing performance was similar to that observed in Na\(_{1}\)-based IDMs, which are in turn compatible with conventional semiconductor technologies. Although the proton conductivity of mesoporous SiO\(_2\) thin films (1.29 \(\times\) 10\(^{-4}\) S cm\(^{-1}\)) is lower than that of Na\(_{1}\) (approx. 10\(^{-2}\) S cm\(^{-1}\)), the mesoporous SiO\(_2\)-based IDMs did, however, exhibit substantially reduced fluctuations in CSR and improved reached CSR compared with Na\(_{1}\)-based IDMs. These differences may be attributed to the chemically stable nature of the mesoporous SiO\(_2\) matrix and its ability to endure the application of repetitive pulse currents, which make it suitable for the achievement of superior decision-making.

### 4. Conclusion

In this study, proton conducting mesoporous SiO\(_2\) thin films were applied to IDM electrolytes to achieve highly-integrated device fabrication and repetitive operations. Excellent MBP solving properties and adaptation to environmental shifts were achieved by the operation of the mesoporous SiO\(_2\)-based IDMs, which are in turn compatible with conventional semiconductor technologies. Their computing performance was similar to that observed in Na\(_{1}\)-based IDMs, which are in turn compatible with conventional semiconductor technologies. Although the proton conductivity of mesoporous SiO\(_2\) thin films (1.29 \(\times\) 10\(^{-4}\) S cm\(^{-1}\)) is lower than that of Na\(_{1}\) (approx. 10\(^{-2}\) S cm\(^{-1}\)), the mesoporous SiO\(_2\)-based IDMs did, however, exhibit substantially reduced fluctuations in CSR and improved reached CSR compared with Na\(_{1}\)-based IDMs. These differences may be attributed to the chemically stable nature of the mesoporous SiO\(_2\) matrix and its ability to endure the application of repetitive pulse currents, which make it suitable for the achievement of superior decision-making.

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