Supplementary Materials for

Ionic decision-maker created as novel, solid-state devices

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Section S1. Fabrication of electrochemical cells for ionic decision-maker

Fig. S1. Fabrication of electrochemical cells for ionic decision-maker.
Section S2. Comparison with CPU-based computation using mathematical algorithms and dielectric capacitor

(i) Comparison with theoretical calculation using the TOW principle
Figure S2(a) shows theoretical calculation using CPU-based computation with the TOW principle. The probabilities of channels A and B (P_A, P_B) were set to (0.8, 0.2). The forgetting parameter, \( \alpha \), was set to 0.95. The calculation shows adaptive behaviour following a \( P_i \) inversion after 200 selections. This behaviour agrees with the experimental results achieved with an electrochemical cell [shown in Fig. 2(b)].

(ii) Comparison with dielectric capacitor
As mentioned in Fig. 2, a simple capacitor is not enough to solve dynamic MBPs. Let us consider what makes our ionic decision-maker device different from simple capacitors and how it functions to solve MBPs. The red curve in the panel of Fig. S2(b) shows the variation in CSR for a dielectric capacitor (with a capacitance of 33 \( \mu F \)) instead of our electrochemical cells measured under the same conditions as for Fig. 2(b). Although the dielectric capacitor showed good performance for the first 200 selections, it showed very poor adaptability after \( P_A \) and \( P_B \) were inverted, in contrast to the rapid and adaptive response of the electrochemical cell (blue curve). The red curve in the lower panel of Fig. S2(b) shows the variation in voltage for the dielectric capacitor. The voltage remained positive even after 200 selections following \( P_i \) inversions while the voltage for the electrochemical cell became negative after about 30 selections following the inversions. This difference in behavior is related to the forgetting parameter, \( \alpha \) (\(<1\) in the TOW principle, as discussed below.\(^{17}\)

In the charge-conserving TOW principle, the variations in the electrical charge applied to the cell \( \Delta Q_i(n) \), are summed up after each selection. Decisions (about which channel to select) are made on the basis of the sum of \( \Delta Q_i(n) \), which is equal to \( Q_i(n) \). However, the charges are processed using \( \alpha \) (\(<1\))

\[
Q_i(n) = \Delta Q_i(n) + \alpha Q_i(n-1)
\]

where \( Q_i(n) \) and \( \Delta Q_i(n) \) are the charge at the \( n \)th selection, and the variation in the charge applied at the \( n \)th selection, respectively.

This is quite an important process because \( \alpha \) works as a discounting parameter giving recent selections more weight in the decision-making as is done in other
algorithms. For example, given \( \alpha \) and \( n \) are 0.95 and 100, the contribution from a variation in the charge at \( n = 1 \) to \( Q_i(n) \), namely \( \alpha^{n-1} \Delta Q_i \), is reduced to as little as 0.6% \( (\alpha^{n-1} = 0.95^{100-1}) \) of that from \( \Delta Q_i(n) \). Accordingly, without the function of \( \alpha \), the TOW principle does not work as an adaptive principle. The black curve in Fig. S2(b) shows the variation in CSR for a TOW simulation with \( \alpha = 1 \), i.e. \( \alpha \) does not work as a weight parameter. It showed poor adaptability, which is similar to the behavior of the dielectric capacitor. This similarity is quite reasonable because the consecutive input of preserved charges (current) to the dielectric capacitor was identical to that to the TOW without the function of \( \alpha \) (<1) in principle. See S2(c) for details.

While \( \alpha \) is usually used in algorithms as a mathematical function, our ionic decision maker inherently includes \( \alpha \). It should thus be termed “built-in \( \alpha \)”. This is a great advantage of the ionic decision-maker because an \( \alpha \) emulation using physical phenomena is crucially important for physical implementation, and such emulation has not been successful so far. See S3 for details of built-in \( \alpha \) and how the function is used in the operation principle.

A difference between the theoretical calculation discussed above and experiments should be noted. While \( Q(n) \) is directly used to make decisions in the theoretical calculation, \( V(n) \), which is varied by the consecutive input of \( Q \), is used instead in experiments. In the case with dielectric capacitor, in which \( Q(n) \) and \( V(n) \) are in linear relationship, variation in \( V(n) \) can be equivalent to that in \( Q(n) \) although the linear relationship is not advantageous for adaptive decision-making at all. In contrast, in the case with electrochemical cells, \( V(n) \) is effectively used to utilize a strong non-linearity in \( Q(n) - V(n) \) relationship which is attained by consuming \( Q \) for electrochemical reactions.

(iii) Comparison with CPU-based computations using mathematical algorithms
The ionic decision-maker operation was compared with CPU-based computations using mathematical algorithms. The red curve in the upper panel of Fig. S2(c) shows the variation in CSR of the ionic decision-maker following a \( P_i \) inversion. The channel probabilities (\( P_A, P_B \)) were set to (0.9, 0.1). The ionic decision-maker device performed 400 consecutive selections, with each selection being repeated for 100 cycles. The CSR of the ionic decision-maker device gradually increased to 1 while it dropped after 200
selections due to the probability inversion. This quick and adaptive behaviour clearly demonstrates that our ionic decision-maker device can solve dynamic MBPs.

Next, we performed a calculation with the SOFTMAX and $\varepsilon$-greedy algorithms, which are the algorithms most commonly used for solving MBPs, for comparison. The two algorithms selected one channel on the basis of experience accumulated through selections. For example, the SOFTMAX algorithm selected channel A when \[ \frac{r_A}{r_A + r_B} \] in the algorithm was higher than \[ \frac{r_B}{r_A + r_B} \] (the expression is simplified here). The $r_A$ and $r_B$ are the probabilities of channels A and B, which are calculated by dividing the number of correct decisions by the number of selections using channel A (B). They are updated after each selection, so the algorithm empirically selects a channel. The $\varepsilon$-greedy selected the channel with the highest reward on the basis of experience, same as in the case with the SOFTMAX algorithm, while it explored unknown channels with a certain probability.

The blue and brown curves in the upper panel of Fig. S2(c) show the results for the SOFTMAX and $\varepsilon$-greedy algorithms. In contrast to the first 200 selections, during which the CSR increased to 1 in the same way as did with ionic decision-maker, the CSR showed poor recovery against probability inversions. This is because $r_A$ and $r_B$ are calculated using all of the selection history before the probability inversion, which are no longer useful for making correct decisions (i.e. it contains incorrect information). Therefore, these algorithms cannot adapt to environmental changes (i.e. dynamic MBPs) in contrast to ionic decision-maker.

The lower panel in Fig. S2(c) shows a comparison of the number of packets transmitted with the ionic decision-maker (experiment), SOFTMAX (calculation) and $\varepsilon$-greedy (calculation). The number of packets (i.e. throughput) for ionic decision-maker was about 72\% larger than those for SOFTMAX and $\varepsilon$-greedy after 400 selections due to the excellent adaptability of the ionic decision-maker, (its mechanism will be discussed in S3). Note that the adaptability of the two mathematical algorithms could be improved by adding a forgetting parameter similar to that in the TOW algorithm. This reflects the importance of emulating of $a$ for physical implementation.
Fig. S2. Comparison with CPU-based computation using mathematical algorithms and dielectric capacitor. (a) Variation in CSR for TOW algorithm calculation ($\alpha=0.95$) following probability inversion after 200 selections. (b, upper panel) Variation in CSR for dielectric capacitor (with capacitance of 33 $\mu$F) instead of electrochemical cell measured under the same conditions as for Fig. 2(b). (b, lower panel) Variation in voltage for dielectric capacitor and electrochemical cell. (c) Variation in CSR for ionic decision-maker, SOFTMAX, and $\varepsilon$-greedy algorithms following probability inversion after 200 selections.
Section S3. Operation mechanism of ionic decision-maker

As long as we deal with selections as stochastic events, it is not easy to compare a theoretical expectation with experimental results. Such a comparison is, however, relatively easy if we assume that selections are quasi-deterministic events (i.e. $P_A$ or $P_B$ is assumed to be 1).

Figure S3(a) shows the $\alpha$ dependence of selection number - charge [i.e. $Q_i(n)$ in eq. (3)] characteristics for a probability inversion from $(P_A, P_B) = (1,0)$ to $(0,1)$. The situation is equivalent to that $\Delta Q_i(n)=1$ for all of the first 100 selections while $\Delta Q_i(n) = -1$ for the next 100 selections.

With $\alpha=1$, the characteristic is calculated to be simply $n$ for 0 to 100 selections and 200 - $n$ after 100 selections. When $\alpha$ is less than 1, eq. (3) can be expressed by using the sum of a geometric progression with an equal ratio of $\alpha$ and an initial term of 1:

$$Q_i(n) = \frac{1-\alpha^n}{1-\alpha}$$ for the first 100 selections, and

$$Q_i(n) = \frac{1-\alpha^n}{1-\alpha} - 2\frac{1-\alpha^{n-100}}{1-\alpha}$$ for the last 100 selections.

One significant feature of the characteristics with small $\alpha$ is that $N_0$, defined as the number of selections at which the curves cross the x-axis (indicated by black arrow for $\alpha=0.99$), is smaller than 200 while $N_0$ for $\alpha=1$ is 200. Furthermore, $N_0$ monotonically decreases as $\alpha$ decreases. This means that adaptability is enhanced by the reduction in $\alpha$ (i.e. a small number of selections is enough to adapt to environmental changes).

To emulate the probability inversion shown in Fig. S3(a), we inverted the polarity of the current applied to the ionic decision-maker device. Figure S3(b) shows the current dependence of the $V$-$t$ ($V$-$n$) characteristic with a current polarity inversion from positive to negative. The non-linearity of the $V$-$t$ characteristics are varied widely with respect to various applied currents (10 nA to 10 $\mu$A). With a small current (e.g. 10 nA), the behaviour agreed well with that in a TOW simulation with a relatively large $\alpha$ (e.g. 0.99) as shown in the inset in Fig. S3(b). On the other hand, with a large current (e.g., 10 $\mu$A), the behaviour agreed well with that in a simulation with a relatively small $\alpha$ (e.g. 0.78).

This is a remarkable coincidence because the two characteristics have completely different origins: the selection number - charge characteristics is the sum of a geometric progression while the $V$-$n$ ($V$-$t$) characteristic shown in Fig. S3(b) is the result of the current-dependent electrochemical phenomena discussed below.
Fig. S3. Operation mechanism and built-in \( \alpha \) of ionic decision-maker. (a) \( \alpha \) dependence of selection number –charge characteristics (calculation) with probability inversion from \((P_A, P_B) = (1,0)\) to \((0,1)\). (b) Current dependence of \( V-t \) (\( V-n \)) characteristics (experiment) with a current polarity inversion from positive to negative. Fitting curves were added to 10 nA, 1 \( \mu \)A, and 10 \( \mu \)A.
With a small current, a EDL charge at the Nafion/Pt-C interface mainly occurs and it immediately causes a steep voltage increase due to the relatively small capacitance of the EDL (e.g. several $\mu$F/cm$^2$)\textsuperscript{19-22}. The situation is illustrated in Figs. S3(c)-(i). A slight deviation occurred due to a small loss by Faradaic current.

With a large current, such a voltage increase exponentially activates electrochemical reactions along a Tafel equation; \[ \log i = \log i_0 + \frac{\alpha n F \eta}{RT} \] in which $i$, $i_0$, $\alpha$, $n$, $F$, and $\eta$ are the applied current, the exchange current of electrochemical reactions, and the transfer coefficient, the number of exchanged electrons, the Faraday constant, and the over-potential, respectively. This means that the increase in $V$ is limited to being relatively small even if the current drastically increases. This applies as long as the rate-limiting step of the reactions is a charge transfer process (e.g. electron donation to protons).

As the electrochemical reactions proceed further, diffusion layers [DLs (e.g. proton depletion layers)] are generated near the Pt-C/Nafion interfaces. The situation is illustrated in Fig. S3(c)-(ii). The DLs reduce the reaction rate (i.e. the reaction rate is limited by ionic diffusion); $V$ gradually increases under the constant current conditions. In contrast, when a current is inverted in this situation, the current quickly removes the DLs due to counter-direction proton transport. Therefore, the strong non-linearity and the built-in $\alpha$ of the ionic decision-maker seen in Fig. S2(b) lower panel and Fig. S3(b) are attributed to the time and current-dependent dynamics of electrochemical process near the interfaces.

Fig. S3. (c) Electrochemical behaviour of ionic decision-maker under small (i) and large (ii) current conditions.
Figure S3(d) shows the variation in built-in $\alpha$ and $N_0$ -100 under various current conditions. By increasing current from 10 nA to 10 µA, both built-in $\alpha$ and $N_0$ -100 can be successfully tuned from 0.99 to 0.78 and from 21.6 to 1.8, respectively. Although small built-in $\alpha$ is beneficial for adaptability, there is a trade-off between adaptability and stability, to some extent. For example, with built-in $\alpha$ of 0.78 and $N_0$ -100 of 1.8 for extremely high adaptability, ionic decision-maker can select the wrong channel with only two exceptional selections. While a relatively wide range of built-in $\alpha$ (0.86 to 0.98, corresponding to $N_0$ -100 of 10 to 80) is useful for various situations, the operation property can be further optimized for specific situations only by changing the current value.

![Graph](image.png)

**Fig. S3.** (d) Variation in built-in $\alpha$ and $N_0$ -100 under various current conditions.
Section S4. Theoretical expectation of decision-making behavior with two devices

In Figs. 3 and 4, two ionic decision-maker devices were operated to emulate decision-making behavior of users 1 and 2 in competitive MBPs. The results agree with behavior expected on the basis of the TOW principle as discussed below. Figure S4 illustrates the expected behavior of the devices and the corresponding variation in selection rates for each channel (i.e. A, B, and C rates, as defined in figure) for both devices. The initial $P_i$ ($P_A, P_B, P_C$) were set to (0.9, 0.4, 0.2). The top panels for devices 1 and 2 represent channels showing the highest $V$ at each selection, which equals the channel selected at the selection. The A rate was calculated by dividing the number of cycles in which the A channel was selected, $N_A$, by the total number of cycles (20 cycles in this case), $C$ (i.e. A rate=$N_A/C$). At the beginning of the operation, the A, B, and C rates for both devices were close to 0.33 (i.e. 1/3), which corresponds to a random distribution. While the A and B rates increased to 0.5, the C rate decreased to zero due to the lowest $P_C$ (0.2), as seen for the 8th selections. The asymptotic approaches of the A and B rates to 0.5 means that both devices selected channel A (with the highest $P_i$) in about half the cycles (ten) while, in the remaining cycles (ten), they selected channel B (with the second highest $P_i$). This was caused by the interaction between the devices, as mentioned above. The A, B, and C rates reach different values due to the different $P_i$ assignments (0.4, 0.2, 0.9) after the 9th selections. Note that the operation described here corresponds to combined operation mode, which will be discussed in S5. In the other operation mode, termed as independent operation discussed in S5, the interaction mentioned above does not work because the two devices are electrically separated during current application.
Fig. S4. Expected behavior of two devices and corresponding variation in selection rates for each channel for both devices.
Section S5. Two operation modes of ionic decision-maker for competitive MBPs with two devices and three channels

Two electrochemical cells were placed in a manual prober system and connected using three tungsten probes, as shown in Fig. 1(d). The cells were connected to a potentiogalvanostat via a switch matrix. The set-up was almost the same as the one described in Materials and Methods. Two operation modes were used.

(i) Independent operation with two users and three channels

In the independent operation mode, the devices did not interact with each other during operation. This means that they were electrically isolated during current application. The operation was composed of 400 consecutive selections, with each selection being repeated for 20 cycles. The initial $P_i$ ($P_A$, $P_B$, $P_C$) were set to (0.9, 0.4, 0.2). Each cycle started with a short-circuit of the six electrodes for 200 s in order to refresh the two ionic decision-maker devices (refreshment stage). The circuit was opened, and the voltages of electrodes A and B (with respect to electrode C) of device 1 were measured to identify the electrode with the highest voltage. When the voltage of electrode A was the highest, channel A was selected. The access was emulated by random number generation with $P_A$, and the current was subsequently applied from electrode A to electrodes B and C for 500 ms. This means that the input currents to electrodes A, B, and C are +1 $\mu$A, -500 nA, and -500 nA, respectively.

After current application to device 1, the circuit of device 1 was opened. The same procedure was then performed for device 2. This successive process corresponds to one access. After every 100 repetitions of the selections, $P_A$, $P_B$ and $P_C$ were changed to emulate environmental changes. After 400 consecutive selections with 3 inversions (i.e., one cycle was finished), the operation moved to the refreshment stage of the next cycle. A total of 20 cycles were performed for each $P_A/P_B/P_C$ combination.

Figure S5(a) shows the variations in the channel selection rate (A, B, and C) for devices 1 and 2. As clearly seen, both devices were always seeking the channel with the highest $P_i$. These results clearly demonstrate that normal ionic decision-maker can select the channels with the highest $P_i$ even if there are more than two channels.

(ii) Combined operation with two devices and three channels

In the combined operation mode, the devices interacted with each other during operation. The operation procedure was similar to that in the independent case. One
difference was that the devices 1 and 2 were electrically connected during current application. The operation was composed of 400 selections, with each selection being repeated for 20 cycles. The initial \( P_i \) (\( P_A, P_B, P_C \)) were set to (0.9, 0.4, 0.2). Each cycle started with a short-circuit of the six electrodes for 200 s in order to refresh the two electrochemical cells (refreshment stage). The circuit was opened and the voltages of electrodes A and B (with respect to electrode C) of device 1 were measured to identify the electrode with the highest voltage. When the voltage of electrode A was the highest, channel A was selected. The selection was emulated by random number generation with \( P_A \) and current was subsequently applied from electrode A to electrodes B and C for 500 ms. This means that the input currents to electrodes A, B, and C were +1 \( \mu A \), -500 nA, and -500 nA, respectively. During current application, electrode A of device 1 was connected to electrode A of device 2. This was accompanied by current application to electrodes A, B, and C of device 2. The input current to electrodes A, B, and C of device 2 were -1 \( \mu A \), +500 nA, and +500 nA, respectively.

Fig. S5. Two operation modes of ionic decision-maker for competitive MBPs with two devices and three channels. (a) Variation in selection rates for channels (A, B, and C) for devices 1 and 2 measured for 20 cycles. Initial probabilities of channels were set to \((P_A, P_B, P_C) = (0.9, 0.4, 0.2)\), and assignment was changed after every 100 selections.
After current application to device 1, the circuit of device 1 was opened. The same procedure was then performed for device 2. This successive process corresponds to one selection. After every 100 repetitions of the selections, $P_A$, $P_B$ and $P_C$ were changed to emulate environmental changes. After 400 consecutive selections with 3 inversions (i.e. one cycle was finished), the operation moved to the refreshment stage of the next cycle. A total of 20 cycles were performed for each $P_A/P_B/P_C$ combination.

As discussed for Fig. 4(a, b), the two devices selected the channels with the highest and second highest $P_i$. The variation in CSR for the devices saturated at 0.5, indicating that they were selecting in the SM manner. The results clearly demonstrate that interactive nanoionic decision-maker can select the channels with the highest and second highest $P_i$.

(iii) Comparison of performance of two operation modes and theoretical limits

The total number of packets for both independent and combined operation mode [shown in Figs. S5(a) and 4(b)] was calculated in almost the same manner as described in Materials and Methods, but the total number for devices was accumulated to obtain the total number.

The performance for independent mode [Fig. S5(a)] was close to that of the theoretical limit for NE because the two devices were attempting to access the highest $P_i$ channel, resulting in a reduction in performance due to access overlap. The performance of the combined mode [Fig. 4(b)] was far beyond that of the independent mode and the theoretical limit for NE. It was quite close to the theoretical limit for SM because the combined devices avoided overlap and achieved SM. The difference in the two operation modes is evident when we define and compare SM rate for the modes, as discussed below.

(iv) Comparison of SM rate of two operation modes

The result shown in Fig. 4(a) suggests that the devices achieved SM because CSR reached 0.5. However, this does not guarantee the situation. SM could not be realized even when the A and B rates were 0.5. In this case, both devices selected channel A in the first ten cycles and then selected B in the remaining cycles.

To distinguish the achievement of SM during operation, we need to compare a selection of both devices in the same cycles. The SM rate is defined as the number of cycles in
which both devices selected the two channels with the highest $P_i$ and the second highest $P_i$ (e.g. channels A and B) in the same cycle, divided by the total number of cycles.

Figure S5(b) illustrates the expected variation in the SM rate with respect to the variation in channel selection, which is identical to that shown in Fig. S4. While channel A was selected at the 5th access in the first cycle for device 1, channel B was selected at the corresponding access for device 2. SM was achieved at the access as indicated by the orange circles. On the other hand, channel A was selected at the 3rd access in the first cycle for both devices, as indicated by the black circles. This is not SM but NE, resulting in a loss in total packets due to the overlapping selection, as illustrated in Table 1. Because SM maximizes the total number of transmitted packets, the SM rate is an index of efficiency of the society [devices (or user) 1 and 2].

The red curve in Fig. S5(c) represents the actual variation in the SM rate between devices 1 and 2, calculated from the results shown in Fig. 4(a). The SM rate repeatedly reached 1.0 even with the $P_i$ assignment changes. This is direct evidence of SM achievement for a competitive DMBP.

For comparison, we also examined the SM rate of the independent devices for the result shown in Fig. S5(a). SM rate is indicated by the blue curve in Fig. S5(c). The independent devices had a very low SM rate because the devices independently sought the highest $P_i$, leading to the NE state. The low SM rate is consistent with the poor performance shown as independent devices in Fig. 4(b). The comparison of SM rate supports that ionic decision-maker with the combined devices is advantageous for solving competitive DMBPs.
Solvability of combined operation for competitive DMBPs with a different $P_i$ combination (0.5, 0.4, 0.2)

To confirm the solvability of the combined operation for competitive DMBPs with a different $P_i$ combination, the initial $P_i (P_A, P_B, P_C)$ were set to (0.5, 0.4, 0.2), for which the highest and second highest $P_i$ were closer than that for the competitive DMBPs discussed in S5(a). The other operation conditions were almost the same as those for competitive DMBPs discussed in S5(a) except for the $P_i$ combinations.

Figure S5(d) shows the variation in the channel selection rates (A, B, and C) for devices 1 and 2. For both devices for the first 100 selections, the A and B rates gradually increased and reached about 0.5 while the C rate decreased to an extremely low level.
This means that devices 1 and 2 selected channel A (with the highest $P$) in about half the cycles while, in the remaining cycles, the devices selected channel B. This variation in behaviour between channels is quite similar to that for the previous competitive DMBPs with $(P_A, P_B, P_C)=(0.9, 0.4, 0.2)$. Figure S5(e) shows the variation in SM rate between devices 1 and 2 corresponding to the results shown in Fig. S5(b). The SM rate repeatedly reached 1.0, evidence that the combined devices successfully solved the competitive DMBPs as well as previous competitive DMBPs.
(d) Variation in selection rates for channels (A, B, and C) for devices 1 and 2 measured for 20 cycles for averaging. Initial probabilities of the channels ($P_A$, $P_B$, $P_C$) were set to (0.5, 0.4, 0.2), and assignment was changed after every 100 selections. (e) Variation in SM rate between user 1 and 2.

**Fig. S5.** (d) Variation in selection rates for channels (A, B, and C) for devices 1 and 2 measured for 20 cycles for averaging. Initial probabilities of the channels ($P_A$, $P_B$, $P_C$) were set to (0.5, 0.4, 0.2), and assignment was changed after every 100 selections. (e) Variation in SM rate between user 1 and 2.