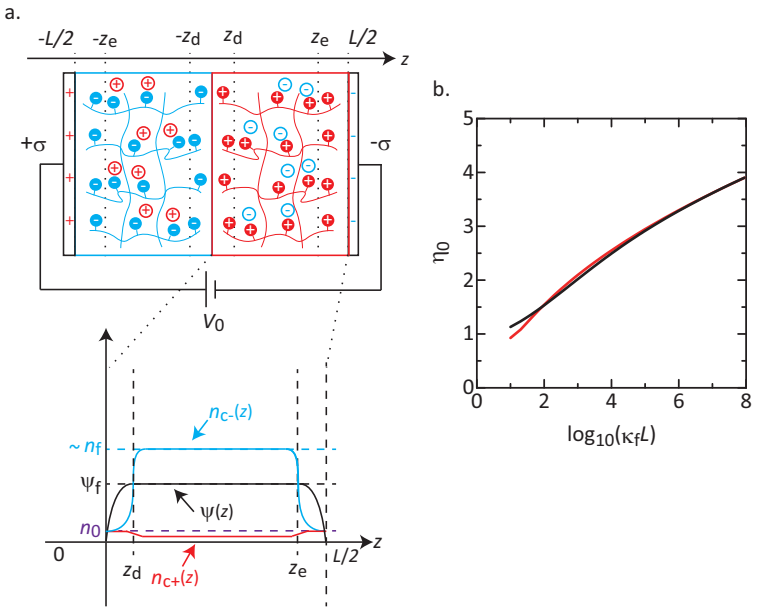

Supplementary Figure 1: Zero of overpotentials: Electrostatic potentials $\psi(z)$ and the local densities, $n_{c+}(z)$ and $n_{c-}(z)$, of positive and negative counterions in a half of polyelectrolyte gel diode (PGD), $z > 0$, are shown schematically for the cases that the two electrodes are short-circuited (a). The profiles of electrostatic potentials are symmetric (with respect to $z = L/4$) because of the fact that the local densities of counterions are distributed with the Boltmann distributions. The zero of overpotentials η_0 is defined by potential drops at the surfaces of the electrodes, $E_{L/2}/\kappa_f$, for the cases that the two electrodes are short-circuited (where $E_{L/2}$ is electric fields at $z = L/2$, rescaled by T/e, and κ_f $(= \sqrt{4\pi l_B n_f})$ is the Debye length due to the electric charges of polyelectrolytes and their counterions), see also Methods in the main article. The zero of overpotentials is shown as functions of the (rescaled) thickness $\kappa_f L$ of the gels, the black solid curve in (b). The red solid curve shows calculations by using an approximate equation (supplementary equation (12)).

Supplementary Note 1: Debye-Huckel approximation

Equation (11) in the main article is treated relatively easily for the cases that there are no hydrogen and hydroxide ions in the system, $n_{\mathrm{H}}(z) = n_{\mathrm{OH}}(z) = 0$. In this case, equation (11) (in the main article) return to Poisson-Boltzmann equation that has the form

$$\frac{\partial^2}{\partial z^2}\psi(z) = \kappa_0^2 \sinh \psi(z) - 4\pi l_{\mathrm{B}} n_{\mathrm{f}} \tag{1}$$

with equations (4) and (5) in the main article, where $\psi(z)$ is electrostatic potentials in the unit of the thermal voltage T/e (T is the absolute temperature in the unit of Boltzmann constant and e is the elementary charge). κ_0 ($\equiv \sqrt{8\pi l_{\mathrm{B}} n_0}$) is the inverse Debye screening length due to freely diffusing counterions (both positive and negative), where n_0 is the local density of positive (or negative) counterions at $z = 0$. n_{f} is the density of ionic groups of polyelectrolyte gels. l_{B} ($\equiv e^2/(4\pi\epsilon T)$) is the Bjerrum length, where ϵ is the dielectic constant of the media (this includes the contributions of polyelectrolyte gels and aqueous solutions and is assumed to be uniform in the entire volume of the system). The geometry of PGDs is shown in fig. 1 of the main article. Because of the symmetry of the system, we treat only a half of the system, $z > 0$.

We here follow the approaches used by Pincus[1] and Yamamoto and Pincus[2]. Equation (1) predicts that electrostatic potentials are approximately constant and have the form

$$\psi_{\mathrm{f}} = \sinh^{-1} \frac{n_{\mathrm{f}}}{2n_0} \tag{2}$$

in the bulk of the gels (see refs. 1 and 2 for details). We thus expand the right-hand-side of supplementary equation (1) in a Taylor series

$$\frac{\partial^2}{\partial z^2}\psi(z) \simeq \kappa_{\mathrm{t}}^2(\psi(z) - \psi_{\mathrm{f}}) \tag{3}$$

with respect to the deviation of electrostatic potentials from the bulk value ψ_{f} and omit

higher order terms (Debye-Huckel approximation), where $\kappa_{\rm t}$ ($\equiv \sqrt{4\pi l_{\rm B} n_{\rm t}}$) is the inverse Debye screening length due to the positive and negative counterions in (the bulk region of) polyelectrolyte gels and $n_{\rm t}$ ($\equiv \sqrt{n_{\rm f}^2 + 4n_0^2}$) is the sum of densities of these positive and negative counterions there. Electrostatic potentials $\psi_{\rm bulk}(z)$ that are derived from the approximate equation (supplementary equation (3)) are effective in the bulk region of the gel, where electrostatic potentials do not greatly deviate from $\psi_{\rm f}$. We thus define this bulk region by $\psi_{\rm bulk}(z) > \psi_{\rm f} - 1$.

In the region, where $\psi(z) < \psi_{\rm f} - 1$, both positive and negative counterions are depleted (depletion layer). To treat electrostatic potentials in depletion layers, we use Debye-Huckel approximation that expands the right-hand-side of supplementary equation (1) in a Taylor series

$$\frac{\partial^2}{\partial z^2}\psi(z) \simeq \kappa_0^2 \psi(z) - \kappa_{\rm f}^2 \tag{4}$$

with respect to electrostatic potentials, where $\kappa_{\rm f}$ ($\equiv \sqrt{4\pi l_{\rm B} n_{\rm f}}$) is the inverse of a length that does not depend on applied voltages. Electrostatic potentials that are effective for depletion layers are denoted as $\psi_{\rm dep}(z)$ and $\psi_{\rm ele}(z)$; the subscripts 'dep' and 'ele' indicate the depletion layers at the interface between the two oppositely charged gels and at the surfaces of the electrode, respectively.

We apply the boundary conditions to these approximate electrostatic potentials; electrostatic potentials are zero at $z = 0$ and electric fields and electrostatic potentials at $z = L/2$ are $E_{L/2}$ and $\psi_{L/2}$, respectively (see also "Steady states and boundary conditions" in the main article). Moreover, approximate electrostatic potentials and electric fields are continuous at the boundaries between the bulk region and the depletion layers, $z = z_{\rm d}$ (and $z = z_{\rm e}$, if any). The position of these boundaries are defined by $\psi_{\rm bulk}(z_{\rm d}) = \psi_{\rm dep}(z_{\rm d}) = \psi_{\rm f} - 1$ and $\psi_{\rm bulk}(z_{\rm e}) = \psi_{\rm ele}(z_{\rm e}) = \psi_{\rm f} - 1$ (see above). This indeed predicts that the local densities of counterions are very small in the depletion layer at the interface between the two gels,

and thus negligible to a good approximation, see also Supplementary Note 6. In contrast, the local densities of counterions are relatively large in the depletion layers at the surfaces of the electrodes (more precisely, in the region of $\psi_{\rm ele}(z) < 0$) because these counterions are attracted directly by electric charges on the electrodes. Bulk electrostatic potentials $\psi_{\rm f}$ (or, equivalently, n_0) are determined by the conservation of the number of counterions − equation (6) in the main article. For a very large applied voltage, counterions may show Gouy-Chapman layers (in which only one type of charges exists and thus Debye-Huckel approximation fails [3]) at the surfaces of the electrodes, but we do not treat them in this paper because they do not play an important role in the ion current rectification of PGDs.

Supplementary Note 2: Electrostatic screening of carrier ions

For the cases that the electrodes show electrochemical reactions, electrostatic potentials and the local densities of hydrogen and hydroxide ions in the bulk region are derived by using equation (9), (10), and (11), in the main article.

For reverse voltages, hydrogen ions diffuse in the bulk of positive polyelectrolyte gels. Because the electric charges of these hydrogen ions generate electrostatic potentials, Poisson equation have the form

$$\frac{\partial^2}{\partial z^2}\psi(z) \simeq \kappa_{\rm t}^2(\psi(z) - \psi_{\rm f}) - 4\pi l_{\rm B} n_{\rm H}(z), \tag{5}$$

see also supplementary equation (3). We formally solve this supplementary equation by treating the local density $n_{\rm H}(z)$ of hydrogen ions as a given function; this leads to the form

$$\psi_{\rm bulk}(z) \simeq \psi_{\rm f} + \frac{\bar{n}_{\rm H}(z)}{n_{\rm t}}, \tag{6}$$

where we did not write out boundary terms, $A_{\rm bulk}{\rm e}^{-\kappa_{\rm t} z} + B_{\rm bulk}{\rm e}^{\kappa_{\rm t} z}$ ($A_{\rm bulk}$ and $B_{\rm bulk}$ are

integral constants that should be determined by the boundary conditons, see Methods in the main article or Supplementary Note 1) because these terms are only significant at the boundaries of the bulk region. $\bar{n}_{\rm H}(z)$ has the form

$$\bar{n}_{\rm H}(z) = \frac{\kappa_{\rm t}}{2} \int dz' n_{\rm H}(z') {\rm e}^{-\kappa_{\rm t}|z-z'|}, \tag{7}$$

where this integral should be performed from $z_{\rm d}$ to $z_{\rm e}$ for the cases that there are depletion layers at the surfaces of the electrodes and from $z_{\rm d}$ to $L/2$ for the cases that there are no depletion layers at these surfaces.

Supplementary equation (7) has the form of the local density of hydrogen ions that is averaged over the Debye length; this implies that electrostatic potentials $\psi(z)$ and the averaged local densities of hydrogen ions $\bar{n}_{\rm H}(z)$ are distributed with a length scale that is larger than the Debye length $\kappa_{\rm t}^{-1}$ (more formal treatment is shown in Supplementary Note 4). We thus replace the local density $n_{\rm H}(z)$ of hydrogen ions in equation (9) to the averaged density $\bar{n}_{\rm H}(z)$ and use supplementary equation (6); this leads to the form

$$J_{\rm H} = -D_{\rm hyd} \left[\frac{\partial}{\partial z} \bar{n}_{\rm H}(z) + \frac{1}{n_{\rm t}} \bar{n}_{\rm H}(z) \frac{\partial}{\partial z} \bar{n}_{\rm H}(z) \right]. \tag{8}$$

This equation has the form of freely diffusing particles that show short-range repulsive interactions that are characterized by the second virial coefficient $n_{\rm t}^{-1}$. With an approximate boundary condition, $\bar{n}_{\rm H}(z_{\rm d}) = 0$ (see Supplementary Note 5), the solution of supplementary equation (8) is derived in the form of equation (1) in the main article.

For forward voltages, hydroxide ions that are generated at the surface of the electrode diffuse in the positive polyelectrolyte gel. With a calculation that is similar to the cases of reverse voltages, electrostatic potentials in the bulk region are derived in the form

$$\psi_{\rm bulk}(z) \simeq \psi_{\rm f} - \frac{\bar{n}_{\rm OH}(z)}{n_{\rm t}}, \tag{9}$$

where we did not write out boundary terms, $A_{\rm bulk}{\rm e}^{-\kappa_{\rm t}z} + B_{\rm bulk}{\rm e}^{\kappa_{\rm t}z}$ ($A_{\rm bulk}$ and $B_{\rm bulk}$ are integral constants that should be determined by the boundary conditions, see Methods and Supplementary Note 1, and their forms are, in general, different from the cases of reverse voltages). $\bar{n}_{\rm OH}(z)$ has the form of the local density of hydroxide ions that is averaged over the Debye length,

$$\bar{n}_{\rm OH}(z) = \frac{\kappa_{\rm t}}{2}\int dz' n_{\rm OH}(z'){\rm e}^{-\kappa_{\rm t}|z-z'|}. \tag{10}$$

With an argument that is similar to the cases of reverse voltages, we replace the local density of hydroxide ions $n_{\rm OH}(z)$ in equation (10), in the main article, to the averaged density $\bar{n}_{\rm OH}(z)$. By using this treatment and supplementary equation (9), the fluxes of hydroxide ions have the form

$$J_{\rm OH} \;=\; -D_{\rm hyd}\left[\frac{\partial}{\partial z}\bar{n}_{\rm OH}(z) + \frac{1}{n_{\rm t}}\bar{n}_{\rm OH}(z)\frac{\partial}{\partial z}\bar{n}_{\rm OH}(z)\right]. \tag{11}$$

With an approximate boundary condition, $\frac{\bar{n}_{\rm OH}(z_{\rm d})}{n_{\rm t}} \simeq \frac{z_{\rm d}}{\lambda_{\rm t}}$ (see Supplementary Note 5), the (averaged) local density of hydroxide ions has the form of equation (3) in the main article. Indeed, for forward voltages, the detail of the boundary conditions gives only minor effects on the final results because most of hydrogen (or hydroxide) ions are distributed in the bulk of the gel, $z_{\rm d} \ll L$ (see also Supplementary Notes 5 and 9).

For both reverse and forward voltages, hydrogen and hydroxide ions are neutralized by the electric charges of the polyelectrolyte gels and their counterions in the bulk region, see supplementary equations (6) and (9). Moreover, the local densities of hydrogen and hydroxide ions are very small in the depletion layers (where the local density of counterions is also very small), see also Supplementary Note 5. In the first approximation, electrostatic potentials in PGDs are generated by the electric charges of the polyelectrolyte gels and their counterions. The functional forms of electrostatic potentials are thus the same as the cases of the equilibrium. However, the values of the thickness $z_{\rm d}$ of the depletion layer and

potential drops $\psi_{\rm f}$ are very different from the cases of the equilibrium (see the main article and Supplementary Notes 8 and 9).

Supplementary Note 3: Zero of overpotentials

The zero of overpotentials η_0 is defined by potential drops $E_{L/2}/\kappa_{\rm f}$ at the surfaces of the electrodes when the two electrodes are short-circuited, $V_0 = 0$, Supplementary Fig. 1 (a). In this case, the two electrodes do not show electrochemical reactions (see "Electrochemical reactions" in the main article) and thus η_0 is derived by using the equations that are shown in Supplementary Notes 6 and 7. The polyelectrolyte gels show depletion layers at the surfaces of the electrodes when applied voltages are zero, see figure 2 in the main text. We thus use supplementary equations (26) and (28) to derive the zero of overpotentials, see the black solid curve in Supplementary Fig. 1 (b). The zero of overpotentials has an approximate form

$$\eta_0 \simeq \left[\log\left(\frac{\kappa_{\rm f}L}{2}\right) - 1 - \log\left(\sqrt{\log\left(\frac{\kappa_{\rm f}L}{2}\right) - 1}\right)\right]^{1/2}, \tag{12}$$

see the red solid curve in Supplementary Fig. 1 (b).

Supplementary Note 4: Formal treatment of transport equations

We here show only the cases of reverse voltages because the cases of forward voltages are treated by using a similar argument. For reverse voltages, the local density of hydrogen ions in the bulk region of the gel is derived by using equation (9) in the main article and supplementary equation (5). Rescaling equation (9) in the main text by $D_{\rm hyd}n_{\rm t}$ leads to the

form

$$\frac{1}{\lambda_{\rm t}} = \frac{d}{dz}\frac{n_{\rm H}(z)}{n_{\rm t}} + \frac{n_{\rm H}(z)}{n_{\rm t}}\frac{d}{dz}\psi(z). \tag{13}$$

Two length scales are involved in supplementary equations (5) and (13) − the Debye screening length $\kappa_{\rm t}^{-1}$ and the diffusion length $\lambda_{\rm t}$ ($\equiv D_{\rm hyd}n_{\rm t}/(-J_{\rm H})$). The diffusion length is much larger than the Debye screening length. We here derive an asymptotic solution of supplementary equations (5) and (13) in the length scale of the diffusion length. By using a rescaled coordinate ζ ($\equiv z/\lambda_{\rm t}$), supplementary equation (5) is rewritten in the form

$$\frac{1}{\kappa_{\rm t}^2\lambda_{\rm t}^2}\frac{d^2}{d\zeta^2}\psi(\zeta) = \psi(\zeta) - \psi_{\rm f} - \frac{n_{\rm H}(\zeta)}{n_{\rm t}}. \tag{14}$$

For the cases that $\kappa_{\rm t}\lambda_{\rm t} \gg 1$, supplementary equation has an asymptotic solution that has the form

$$\psi(z) = \psi_{\rm f} + \frac{n_{\rm H}(z)}{n_{\rm t}} + \mathcal{O}\left(\frac{1}{\kappa_{\rm t}^2\lambda_{\rm t}^2}\right), \tag{15}$$

where $\mathcal{O}(1/(\kappa_{\rm t}^2\lambda_{\rm t}^2))$ is the terms that are in the order of $1/(\kappa_{\rm t}^2\lambda_{\rm t}^2)$ and we omit these higher order terms. This is indeed equivalent to supplementary equation (6) because supplementary equation (15) treats an asymptotic form of $n_{\rm H}(z)/n_{\rm t}$ that is effective in the length scale of the diffusion length (this is thus equal to the form of $n_{\rm H}(z)/n_{\rm t}$ that is averaged over the Debye screening length, see also supplementary equation (7)). Substituting supplementary equation (15) into equation (9) in the main article leads to the form of supplementary equation (8).

Supplementary Note 5: Boundary conditions for the local densities of carrier ions

We here show that the local densities of hydrogen and hydroxide ions are very small in the depletion layer (at the interface between the two oppositely charged gels) for both reverse and forward voltages. Electrostatic potentials and electric fields are thus generated by the fixed charges of the polyelectrolyte gels and have the form that is the same as the cases of the equilibrium (although the values of the thickness $z_{\rm d}$ of the depletion layer and potential drops $\psi_{\rm f}$ across it are very different, see the main article and Supplementary Notes 8 and 9). We derive the approximate boundary conditions of the local density of the hydrogen ions (for reverse voltages) and hydroxide ions (for forward voltages) at the boundary, $z = z_{\rm d}$, of the depletion layer.

For reverse voltages, hydrogen ions that have positive charges diffuse from the electrodes at $z = L/2$ towards a depletion layer at the interface between the two oppositely charged gels (via the positively charged gel). The local density $n_{\rm H}(z)$ of hydrogen ions in the depletion layer is derived by using equation (9) and (11) in the main article, with the absorbing boundary condition at the center of the system, $n_{\rm H}(0) = 0$. The local density of hydrogen ions in the depletion layer is much smaller than the density of ionic groups of polyelectrolyte gels due to repulsive electrostatic interactions between hydrogen ions and the positive polyelectrolyte gel (where the electric charges of the positive polyelectrolyte gel are not neutralized by negative counterions in the depletion layer). The contributions of the positive charges of hydrogen ions to Poisson equation (11) (in the main article) is thus negligible in the first approximation. With this approximation, electrostatic potentials in the depletion layer have the same form as the cases of the equilibrium and thus equations (9) and (11) in the main article have a solution

$$\frac{n_{\rm H}(z)}{n_{\rm t}} = \frac{1}{\kappa_{\rm f}\lambda_{\rm t}}\sqrt{\frac{\pi}{2}}{\rm e}^{\frac{1}{2}(\kappa_{\rm f}z+E_0/\kappa_{\rm f})^2}\left[{\rm Erf}\left(\frac{\kappa_{\rm f}z+E_0/\kappa_{\rm f}}{\sqrt{2}}\right)-{\rm Erf}\left(\frac{E_0/\kappa_{\rm f}}{\sqrt{2}}\right)\right], \tag{16}$$

where E_0 ($\equiv E(0)$) is electric fields at the center of the system, $z = 0$ and $\mathrm{Erf}(x)$ is the Gauss error function. λ_t ($\equiv D_\mathrm{hyd} n_\mathrm{t}/(-J_\mathrm{H})$) is the diffusion length (see also the discussion below supplementary equation (33) for the physical meaning of this length scale).

The local density of hydrogen ions that is evaluated by using supplementary equation (16) at $z = z_\mathrm{d}$ (that is the position of the boundary of the depletion layer) gives the boundary condition for the local density of hydrogen ions in the bulk region, because the local density of hydrogen ions is continuous at $z = z_\mathrm{d}$. By using the fact that electric fields E_0 are relatively large, $E_0/\kappa_\mathrm{f} \ll -1$ and electric fields are continuous at $z = z_\mathrm{d}$ (and thus $\kappa_\mathrm{f} z_\mathrm{d} + E_0/\kappa_\mathrm{f} \simeq -1$), the local density of hydrogen ions at $z = z_\mathrm{d}$ has an asymptotic form

$$\kappa_\mathrm{f}\lambda_\mathrm{t}\frac{n_\mathrm{H}(z_\mathrm{d})}{n_\mathrm{t}} \simeq \sqrt{\frac{\mathrm{e}\pi}{2}}\left(1 - \mathrm{Erf}\left(\frac{1}{\sqrt{2}}\right)\right) \simeq 0.656. \tag{17}$$

We treat the local density of hydrogen ions in the bulk region in a length scale that is larger than the Debye screening length, κ_t^{-1}. In this length scale, $1/(\kappa_\mathrm{f}\lambda_\mathrm{t}) \sim 0$, see equation (1) in the main article. We thus apply an approximate boundary condition $\bar{n}_\mathrm{H}(z_\mathrm{d})/n_\mathrm{t} = 0$ to the local density of hydrogen ions in the bulk region.

For forward voltages, hydroxide ions are generated at the surfaces of the electrode, $z = L/2$, and are transported (via the bulk of the positive polyelectrolyte gel) to the depletion layer at the interface between the two oppositely charged gels. The local density $n_\mathrm{OH}(z)$ of hydroxide ions in this depletion layer is derived by using equations (10) and (11) in the main article (with $n_\mathrm{H}(z) = 0$). The local density of hydroxide ions is much smaller than the density n_f of ionic groups of the polyelectrolyte gel in the depletion layer (because of the absorbing boundary condition that is enforced at $z = 0$) and its contribution to the Poisson equation (11) is negligible in the first approximation. With this approximation, electrostatic potentials in the depletion layer have the same form as the cases of the equilibrium and thus

equations (10) and (11) in the main article have an approximate solution

$$\frac{n_{\rm OH}(z)}{n_{\rm t}} = \frac{1}{\kappa_{\rm f}\lambda_{\rm t}} {\rm e}^{-\frac{1}{2}(\kappa_{\rm f} z + E_0/\kappa_{\rm f})^2} \sqrt{\frac{\pi}{2}} \left[{\rm Erfi}\left(\frac{\kappa_{\rm f} z + E_0/\kappa_{\rm f}}{\sqrt{2}} \right) - {\rm Erfi}\left(\frac{E_0}{\sqrt{2}\kappa_{\rm f}} \right) \right], \tag{18}$$

where E_0 is electric fields at $z = 0$ (rescaled by the thermal voltage, T/e) and Efri(x) is the imaginary error function. At the vicinity of $z = 0$, supplementary equation (18) is expanded in a Taylor series

$$\kappa_{\rm f}\lambda_{\rm t}\frac{n_{\rm OH}(z)}{n_{\rm t}} \simeq \kappa_{\rm f} z - \frac{1}{2}\frac{E_0}{\kappa_{\rm f}}(\kappa_{\rm f} z)^2 - \frac{1}{3}\left(1 - \frac{1}{2}\frac{E_0^2}{\kappa_{\rm f}^2}\right)(\kappa_{\rm f} z)^3 + \cdots . \tag{19}$$

The local density $n_{\rm OH}(z)$ that is evaluated by supplementary equation (19) at $z = z_{\rm d}$ (the position of the boundary of the depletion layer) give the boundary condition for the local density of hydroxide ions in the bulk region, because the local density of hydroxide ions is continuous at this position. We thus use an approximate boundary condition

$$\frac{n_{\rm OH}(z_{\rm d})}{n_{\rm t}} \simeq \frac{z_{\rm d}}{\lambda_{\rm t}} \tag{20}$$

that is derived by using supplementary equation (19) and omitting higher order terms.

Indeed, the higher order terms of supplementary equation (19) are not necessarily small for the cases that (forward) applied voltages are relatively small (and thus the thickness $z_{\rm d}$ of the depletion layer is relatively large) due to attractive electrostatic interactions between hydroxide ions and the positive polyelectrolyte gel. The local density of hydroxide ions in the bulk region is derived by taking into account these higher order terms in the form (see below)

$$\frac{\bar{n}_{\rm OH}(z)}{n_{\rm t}} \simeq \sqrt{1 + \frac{2(z - z_{\rm d}^*)}{\lambda_{\rm t}}} - 1, \tag{21}$$

where $z_{\rm d}^*$ is an effective thickness that is defined by $z_{\rm d}^* \equiv z_{\rm d} - \lambda_{\rm t} n_{\rm OH}(z_{\rm d})/n_{\rm t}$ ($n_{\rm OH}(z_{\rm d})/n_{\rm t}$

is the local density of hydroxide ions that is evaluated by supplementary equation (18) at $z = z_{\rm d}$). The continuity of the local density of hydrogen ions at $z = z_{\rm d}$ is ensured by the fact that $n_{\rm OH}(z_{\rm d})/n_{\rm t} \ll 1$. However, the effective thickness $z_{\rm d}^*$ gives only minor effects on the final results because it is much smaller than the thickness of the gel, $|z_{\rm d}^*| \ll L/2$; the number of hydrogen ions in the bulk of the gel dominates the number of hydrogen ions in the depletion layer, see also supplementary equation (38).

Supplementary Note 6: Some results of Debye-Huckel approaches

We first treat relatively simple cases that electrochemical reactions at the electrodes are suppressed, $n_{\rm H}(z) = n_{\rm OH}(z) = 0$. However, indeed, electrostatic potentials that are generated by hydrogen and hydroxide ions are very small because the electric charges of these carrier ions are neutralized by the electric charges of polyelectrolytes and their counterions (see also supplementary equations (6) and (9)). Supplementary equations that are shown here are thus still effective even for the cases that electrochemical reactions at the electrodes generate hydrogen and hydroxide ions, to a good approximation.

The treatment in Supplementary Note 1 leads to the thickness of the depletion layers at the interface between the two oppositely charged gels in the form

$$\frac{\kappa_0 z_{\rm d}}{2} = \tanh^{-1}\left[\frac{\sqrt{\cosh\psi_{\rm f} + (\psi_{\rm f}-1)(2\sinh\psi_{\rm f} - (\psi_{\rm f}-1))} - \sqrt{\cosh\psi_{\rm f}}}{2\sinh\psi_{\rm f} - (\psi_{\rm f}-1)}\right], \qquad (22)$$

where this supplementary equation is derived by using the fact that the boundary of the depletion layer is defined by the position, where electrostatic potentials are $\psi_{\rm f} - 1$. The inside of the square bracket in supplementary equation (22) is smaller than unity for any values of $\psi_{\rm f}$. Moreover, for the cases of polyelecrolyte gels that have large enough thickness, bulk electrostatic potentials $\psi_{\rm f}$ are somewhat larger than unity, see, for example, fig. 2 of

the main article, and thus $2\sinh\psi_{\rm f}$ is much larger than $\psi_{\rm f}-1$. In this case, the thickness $z_{\rm d}$ of the depletion layer thus has an approximate form

$$\kappa_{\rm f} z_{\rm d} \simeq \sqrt{2\psi_{\rm f} - 2 + \frac{1}{\tanh\psi_{\rm f}}} - \frac{1}{\sqrt{\tanh\psi_{\rm f}}}, \tag{23}$$

where we tentatively defined an inverse length, $\kappa_{\rm f}$ ($\equiv\sqrt{4\pi l_{\rm B} n_{\rm f}}$), that does not depend on applied voltages; this is the inverse Debye length $\kappa_{\rm t}$ in the bulk of polyelectrolyte gels for $n_0 \to 0$. With this approximation, electrostatic potentials that are generated by counterions in the depletion layer are neglected. Supplementary equation (23) implies that PGDs show depletion layers at the interface between the two oppositely charged gels for the cases that $\psi_{\rm f}$ are larger than unity (one can derive the same result from supplementary equation (22)).

The thickness of the depletion layer at the surface of the electrode have the form

$$\frac{\kappa_0}{2}\left(\frac{L}{2} - z_{\rm e}\right) = \tanh^{-1}\left[\frac{\sqrt{(\psi_{\rm f} - 1 - \sinh\psi_{\rm f})^2 - \cosh\psi_{\rm f} + E_{L/2}^2/\kappa_0^2} + \psi_{\rm f} - 1 - \sinh\psi_{\rm f}}{\sqrt{\cosh\psi_{\rm f}} + E_{L/2}/\kappa_0}\right], \tag{24}$$

where, to derive this form, we used the solutions of approximate Poisson equations, (3) and (4), and the fact that the boundary of this depletion layer, $z = z_{\rm e}$, is defined by the position, at which electrostatic potentials are $\psi_{\rm f} - 1$ ($z_{\rm d} < z_{\rm e}$). $E_{L/2}$ is electric fields at $z = L/2$ (rescaled by the thermal voltage T/e and thus have the dimension of inverse length). Eq. (24) implies that PGDs show depletion layers at the surfaces of the electrodes for the cases that $E_{L/2}/\kappa_{\rm f} > (\tanh\psi_{\rm f})^{-1/2} \simeq 1$.

For the cases that there are no depletion layers at the surface of the electrode at $z = L/2$, electrostatic potentials $\psi_{L/2}$ at this electrode have the form

$$\psi_{L/2} = \psi_{\rm f} - \frac{E_{L/2}}{\kappa_{\rm t}}. \tag{25}$$

For the cases that there is a depletion layer at the surface of the electrode at $z = L/2$,

electrostatic potentials $\psi_{L/2}$ at this electrode have the form

$$\psi_{L/2} = \sinh\psi_{\rm f} - \sqrt{(\sinh\psi_{\rm f} - (\psi_{\rm f} - 1))^2 - \cosh\psi_{\rm f} + E_{L/2}^2/\kappa_0^2}. \tag{26}$$

Supplementary Note 7: Potential drops at the gel-gel interfaces in the equilibrium

We here treat the cases that electrochemical reactions at the electrodes are suppressed, $n_{\rm H}(z) = n_{\rm OH}(z) = 0$. For the cases that there are no depletion layers at the surfaces of the electrodes, the conservation of the number of counterions, equation (6) in the main article, has an approximate form

$$\frac{\kappa_{\rm f} L}{2}\tanh\psi_{\rm f} \simeq \kappa_{\rm f}\left(\frac{L}{2} - z_{\rm d}\right) - \tanh^{3/2}\psi_{\rm f} - \frac{E_{L/2}}{\kappa_{\rm f}}\tanh^2\psi_{\rm f}, \tag{27}$$

where we expanded the integrand of equation (6), in the main article, in a Taylor series with respect to the deviation of electrostatic potentials from the bulk value $\psi_{\rm f}$, omitting the higher order terms, and integrated from $z_{\rm d}$ to $L/2$. The thickness $z_{\rm d}$ is given by supplementary equation (23). We neglected small number of counterions in the depletion layer at the interface between the two gels.

For the cases that there are depletion layers at the surface of the electrodes, the conservation of the number of counterions has an approximate form

$$\frac{\kappa_{\rm f} L}{2}\tanh\psi_{\rm f} \simeq \kappa_{\rm f}(z_{\rm e} - z_{\rm d}) - 2\tanh^{3/2}\psi_{\rm f} + \frac{\kappa_{\rm f} N_{\rm ele}}{2n_0\cos\psi_{\rm f}}, \tag{28}$$

where we derived this equation by expanding the integrand of equation (6) in a Taylor series with respect to the deviation of electrostatic potentials from the bulk value, omitting higher order terms, and integrating from $z_{\rm d}$ to $z_{\rm e}$ (in a similar manner to the derivation of supplementary equation (27)). $N_{\rm ele}$ is the number of counterions in the depletion layer at

the surface of the electrode and has the form

$$\begin{aligned}\frac{N_{\rm ele}}{2n_0} &= -\left(\frac{L}{2}-z_{\rm e}\right)\sinh\psi_{\rm f}+\frac{1}{\kappa_0}\left(\frac{E_{L/2}}{\kappa_{\rm f}}\tanh\psi_{\rm f}-\sqrt{\tanh\psi_{\rm f}}\right)\\ &\quad -\frac{1}{\kappa_0}\left[\sqrt{2\sinh\psi_{\rm f}(\psi_{\rm f}-1)+\cosh\psi_{\rm f}-(\psi_{\rm f}-1)^2}-\sqrt{\cosh\psi_{\rm f}}\right]. \qquad (29)\end{aligned}$$

The first and second terms of supplementary equation (29) are the number of counterions in the depletion layer at the surface of the electrode, $z_{\rm e} < z < L/2$. The last term of this equation subtracts small number of counterions in the region of $\psi_{\rm ele}(z) > 0$ to be numerically consistent with the approximation that neglects counterions in the depletion layer at the interface between the two gels and thus is not important, see the discussion below supplementary equations (22) and (27); counterions in the depletion layer show relatively large effects on the potential drops at the surface of the electrode, see supplementary equation (26), but the number $N_{\rm ele}$ of these counterions is only small. We derived fig. 2 in the main article by using supplementary equations (25) and (27) for $E_{L/2}/\kappa_{\rm f} < 1$ and supplementary equations (26) and (28) for $E_{L/2}/\kappa_{\rm f} > 1$.

Supplementary equation (27) has an asymptotic solution

$$\psi_{\rm f} \simeq \frac{1}{2}\log(\kappa_{\rm f}L)-\frac{1}{2}\log\left(\sqrt{\log(\kappa_{\rm f}L)-1}+\frac{E_{L/2}}{\kappa_{\rm f}}\right) \qquad (30)$$

for $E_{L/2}/\kappa_{\rm f} > -\frac{1}{2}\sqrt{\log(\kappa_{\rm f}L)-1}$; this equation is derived by using the fact that bulk electrostatic potentials $\psi_{\rm f}$ are relatively large (for the cases that $\kappa_{\rm f}L \gg 1$) and thus $\tanh\psi_{\rm f} \simeq 1-2{\rm e}^{-2\psi_{\rm f}}$. The number of counterions in the depletion layer are relatively small and thus supplementary equation (30) is still effective for the cases that there is a depletion layer at the surface of the electrode, $z = L/2$, to a good approximation. For $E_{L/2}/\kappa_{\rm f} < -\frac{1}{2}\sqrt{\log(\kappa_{\rm f}L)-1}$, supplementary equation (27) has another asymptotic solution

$$\psi_{\rm f} \simeq \frac{1}{2}+\frac{1}{2}\frac{E_{L/2}^2}{\kappa_{\rm f}^2}. \qquad (31)$$

Supplementary Note 8: Potential drops at the gel-gel interfaces in the no salt regime − reverse voltages

We here derive the form of the thickness $z_{\rm d}$ of the depletion layer at the interface between the two gels and potential drops $\psi_{\rm f}$ across it by explicitly evaluating the conservation of the number of counterions, see equation (6) in the main article.

There are depletion layers at the surfaces of the electrodes for reverse applied voltages that are smaller than a threshold value (that depends on the rescaled thickness $\kappa_{\rm f}$ and the length λ_0 ($\equiv D_{\rm hyd} n_{\rm f}/J_0$)). However, the threshold voltage is, in general, relatively small and thus most of the cases, there are no depletion layers at the surfaces of the electrodes. In these cases, the conservation of the number of counterions has an approximate form

$$\frac{\kappa_{\rm f} L}{2} \tanh \psi_{\rm f} \simeq \kappa_{\rm f} \left(\frac{L}{2} - z_{\rm d} \right) - \tanh^{3/2} \psi_{\rm f} - \frac{E_{L/2}}{\kappa_{\rm f}} \tanh^2 \psi_{\rm f} + \frac{\kappa_{\rm f} N_{\rm H}}{n_{\rm t}} \tanh \psi_{\rm f} \tag{32}$$

where this equation is derived by expanding the integrand of equation (6) in the main article in a Taylor series with respect to the deviation of electrostatic potentials from the bulk value $\psi_{\rm f}$, omitting higher order terms, and integrating this approximate integrand from $z_{\rm d}$ to $L/2$. $N_{\rm H}$ is the number of hydrogen ions in the bulk of the gels and has the form

$$\begin{aligned} \frac{N_{\rm H}}{n_{\rm t}} &= \int_{z_{\rm d}}^{L/2} dz \frac{\bar{n}_{\rm H}(z)}{n_{\rm t}} \\ &= \frac{\lambda_{\rm t}}{3} \left[\left(1 + \frac{2(L/2 - z_{\rm d})}{\lambda_{\rm t}} \right)^{3/2} - 1 \right] - \left(\frac{L}{2} - z_{\rm d} \right), \end{aligned} \tag{33}$$

where we used equation (1) in the main article to derive the last form of supplementary equation (33). $\lambda_{\rm t}$ ($\equiv D_{\rm hyd} n_{\rm t}/(-J_{\rm H})$) is the length scale that characterizes the distribution of hydrogen ions in the polyelectrolyte gel. The length $\lambda_{\rm t}$ is called diffusion length in this paper because this is indeed the length scale, where the transport processes of hydrogen ions are dominated by diffusion. We derived bulk electrostatic potentials $\psi_{\rm f}$ by using supplementary

equation (32) and use supplementary equation (25) to derive fig. 3 (a) in the main article. (Indeed, we took into account electrostatic potentials that are generated from the positive charges of hydrogen ions, see the second term of supplementary equation (6), in the calculations of fig. 3 (a) in the main article, but these electrostatic potentials are very small and negligible. Moreover, in these calculations, we also treated the depletion layer at the surface of the electrode for the cases that applied voltages are smaller than a threshold value, see also Supplementary Note 6, but the threshold voltage is small.)

For relatively large reverse voltages, bulk electrostatic potentials are very large and thus $\tanh\psi_{\rm f} \simeq 1$. Supplementary equation (32) thus has an approximate solution

$$\kappa_{\rm f} z_{\rm d} \simeq \frac{\kappa_{\rm f} L}{2} - \frac{\kappa_{\rm f}\lambda_{\rm f}}{2}\left[\left(1 + \frac{3}{\kappa_{\rm f}\lambda_{\rm f}}\left(\frac{\kappa_{\rm f} L}{2} + 1 + \frac{E_{L/2}}{\kappa_{\rm f}}\right)\right)^{2/3} - 1\right], \tag{34}$$

where the length $\lambda_{\rm f}$ is defined by $D_{\rm hyd} n_{\rm f}/(-J_{\rm H})$ and this length is much larger than the thickness $L/2$ of the gels because reverse currents are very small. We thus expand supplementary equation (34) in a Taylor series with respect to $L/\lambda_{\rm f}$; this leads to the form

$$\kappa_{\rm f} z_{\rm d} \simeq -\frac{E_{L/2}}{\kappa_{\rm f}} + \frac{1}{8}\frac{\kappa_{\rm f} L^2}{\lambda_{\rm f}} - 1. \tag{35}$$

Bulk electrostatic potentials $\psi_{\rm f}$ are derived by substituting supplementary equation (35) into supplementary equation (23) with an approximation, $\tanh\psi_{\rm f} \simeq 1$.

For relatively small reverse voltages, one can use approximation $\tanh\psi_{\rm f} \simeq 1$ for the right-hand-side of supplementary equation (32), but not for the left-hand-side of this equation because the prefactor $\kappa_{\rm f} L/2$ is, in general, a very large value. With this approximation, bulk electrostatic potentials have an approximate form

$$\psi_{\rm f} \simeq \frac{1}{2}\log(\kappa_{\rm f} L) - \frac{1}{2}\log\left(\sqrt{\log(\kappa_{\rm f} L) - 1} + \frac{E_{L/2}}{\kappa_{\rm f}} - \frac{1}{8}\frac{\kappa_{\rm f} L^2}{\lambda_{\rm f}}\right). \tag{36}$$

Supplementary equation (36) returns to supplementary equation (30) for the cases that the

fluxes of hydrogen ions are zero.

Supplementary Note 9: Potential drops at the gel-gel interfaces in the no salt regime − forward voltages

The conservation of the number of counterions, equation (7) in the main article, has an approximate form

$$\frac{\kappa_{\rm f} L}{2}\tanh\psi_{\rm f} \simeq \kappa_{\rm f}(z_{\rm e}-z_{\rm d}) - 2\tanh^{3/2}\psi_{\rm f} + \frac{\kappa_{\rm f} N_{\rm ele}}{2n_0\cos\psi_{\rm f}} - \frac{\kappa_{\rm f} N_{\rm OH}}{n_{\rm t}}\tanh\psi_{\rm f}, \tag{37}$$

where this equation is derived by expanding the integrand of equation (7), in the main article, in a Taylor series with respect to the deviation of electrostatic potentials from the bulk value $\psi_{\rm f}$, omitting higher order terms, and integrating this approximate integrand from $z_{\rm d}$ to $z_{\rm e}$. $z_{\rm d}$ and $z_{\rm e}$ is derived by using supplementary equations (23) and (24). The form of $N_{\rm ele}$ is shown in supplementary equation (29). $N_{\rm OH}$ is the total number of hydroxide ions in the bulk of the gel and thus has the from

$$\begin{aligned}\frac{N_{\rm OH}}{n_{\rm t}} &= \int_{z_{\rm d}}^{z_{\rm e}} \frac{\bar{n}_{\rm OH}(z)}{n_{\rm t}} \\ &\simeq \frac{\lambda_{\rm t}}{3}\left[\left(1+\frac{L}{\lambda_{\rm t}}\right)^{3/2}-1\right] - \frac{L}{2},\end{aligned} \tag{38}$$

where we used the fact that the thickness of the depletion layer at the interface between the two gels is much smaller than the diffusion length, $z_{\rm d} \ll \lambda_{\rm t}$, and the thickness of the depletion layers at the surfaces of the electrodes are much smaller than the thickness of the gel, $z_{\rm e} \simeq L/2$ (see also the discussion below supplementary equation (21)). We derived bulk electrostatic potentials $\psi_{\rm f}$ by numerically calculating supplementary equation (37) and use supplementary equation (26) to derive fig. 3 (b), in the main article (indeed, electrostatic potentials that are generated by hydroxide ions, the second term of eq. (4) in the main article,

are taken into account in the calculations of fig. 3 (b), but these electrostatic potentials are very small and thus negligible).

Indeed, the second and third terms of the right-hand-side of supplementary equation (37) are much smaller than the last term and the first term, $\kappa_{\rm f}(z_{\rm e}-z_{\rm d})$ (that is approximately $\kappa_{\rm f}L/2$), for the cases that electric currents are relatively large. With these approximations, bulk electrostatic potentials have an approximate form

$$\psi_{\rm f} \simeq \tanh^{-1}\left[\frac{\lambda_{\rm f}}{L}\left\{\left(1+\frac{3}{2}\frac{L}{\lambda_{\rm f}}\right)^{2/3}-1\right\}\right], \tag{39}$$

where the length $\lambda_{\rm f}$ is $D_{\rm hyd}n_{\rm f}/(-J_{\rm OH})$. Substituting supplementary equation (39) into supplementary equation (26) leads to the form of electrostatic potentials at $z=L/2$ (that are indeed the negative of halves of applied voltages, $-V_0/2$) as functions of the fluxes $J_{\rm OH}$ of hydroxide ions.

Supplementary Note 10: Scaling argument for reverse voltages in the equilibrium

We here treat the cases that electrochemical reactions are suppressed, $n_{\rm H}(z)=n_{\rm OH}(z)=0$. For reverse voltages, see fig. 1 (a), in the main article, positive charges σ are induced on the electrode at $z=L/2$. Because negative counterions are recruited from the interface between the two gels to neutralize positive charges on the electrodes, $en_{\rm f}z_{\rm d}\simeq\sigma$, the thickness of the depletion layer is $z_{\rm d}\simeq-\frac{E_{L/2}}{\kappa_{\rm f}^2}$, where $E_{L/2}$ ($\equiv -e\sigma/(\epsilon T)$) is electric fields at $z=L/2$ (that are rescaled by the thermal voltage T/e). Potential drops across the depletion layer are thus $\psi_{\rm f}\simeq\int_0^{z_{\rm d}}dz\frac{e^2n_{\rm f}}{\epsilon T}z\simeq\frac{E_{L/2}^2}{2\kappa_{\rm f}^2}$. Electrostatic potentials at $z=L/2$ are $\psi_{L/2}\simeq\psi_{\rm f}-\frac{E_{L/2}}{\kappa_{\rm t}}$, see supplementary equation (25), because there are no depletion layers at the surfaces of the electrodes for relatively large reverse voltages. Moreover, for large reverse voltages, the local density of positive counterions is very small in the region of the positive polyelectrolyte gel,

$\kappa_t \simeq \kappa_f$, and thus $\psi_{L/2} \simeq \psi_f + \sqrt{2\psi_f}$. Inversing this equation leads to $\psi_f \simeq -V_0/2 + 1 - \sqrt{1 - V_0}$, for $V_0 < 0$, where we used the fact that electrostatic potentials $\psi_{L/2}$ at $z = L/2$ are the negative of halves of applied voltages, $\psi_{L/2}$ $(= -V_0/2)$.

Supplementary Discussion

Our theory predicts that the asymmetry of electric currents increases (forward currents increase and reverse currents decrease) with decreasing the values of $\kappa_f\lambda_0$ $(\sim n_f^{3/2})$; $\kappa_f\lambda_0$ is thus an important parameter that determines the performance of PGDs. At a first glance, this prediction may look counter-intuitive because the electrostatic effects of polyelectrolyte gels would decrease with decreasing the density of their ionic groups. Our theory predicts that the number of hydrogen and hydroxide ions that are accumulated in the gels increases with decreasing $\kappa_f\lambda_0$, see equations (1) and (3), in the main article. The electric charges of these carrier ions are neutralized by the electric charges of polyelectrolyte gels or their counterions and this dramatically changes the distributions of electrostatic potentials in the systems. These electrostatic potentials greatly suppress electric currents for reverse voltages and enhance electric currents for forward voltages, fig. 3 in the main article. This mechanism operates as long as electrostatic interactions between polyelectrolyte gels and their counterions dominate the translational entropy of these counterions (see Methods in the main article).

Supplementary References

(1) Pincus, P. Colloid Stabilization with Grafted Polyelectrolytes. *Macromolecules* **24**, 2912-2919 (1991).

(2) Yamamoto, T. & Pincus, P. A. Collapse of polyelectrolyte brushes in electric fields. *EPL* **95**, 48003 (2011).

(3) Safran, S. A. *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Westview Press, 2003).