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Characterization of ion separation in electrodialysis membranes using $\mathbf{H}_{\mathbf{E}}^{\bar{\beta}}$, a dimensionless number

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ABSTRACT

In electrodialysis membranes (EDMEMs), electric potential gradient serves primarily as driving force to separate ions in electrolyte solutions using anion and cation exchange membranes. Nevertheless, the mere increase in electric potential gradient would not straightforwardly correspond to higher efficiency. Instead, the orientation of electric field lines, in combination with those of the main fluid flow stream, plays a prevailing role. In the present study, a new dimensionless number is proposed, which characterizes the orientation of electric field lines and their effect on the separation process. The dimensionless number would also serve as an engineering design tool which describes the effectiveness of different EDMEM stacks under different operating conditions i.e. velocity or geometrical aspects i.e. dimension of electrodes and membranes.

Keywords: Electrodialysis; Membrane; Ion separation; Electric field; Electric field orientation; Ion mobility

1. Introduction

The utilization of electrodialysis membranes (EDMEMs) is gaining increased attention for various applications. Among them are small- and medium-size desalination plants for villages, hotels, hospitals, and local camps; water reuse for industries; demineralization and ultrapure water treatment required for special industries like semiconductor, chemical, and food industries; and glycerin purification for antifreeze. In light of such high level of demand, characterization and the enhanced performance of EDMEMs would inevitably have great practical implications.

The study of the electric field characteristics in an EDMEM is imperative for analyzing and designing of the whole stack. Furthermore, such study would also explain the deterioration of the EDMEM performance due to the design aspects, e.g. geometrical factors and physical properties of electrolytes and spacers, or due to the development of scaling in terms of pore blockage, deposition layer, or gel formation.

In EDMEMs, electrical potential gradient acts as driving force to separate ions of electrolyte solutions

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using membranes carrying fixed positive charges, i.e. anion exchange membrane (AEM), and fixed negative charges, i.e. cation exchange membrane (CEM). Two dominant and interactive forces of fluid flow and electric fields affect the extent of ion separation, then movement of ions from one electrode to another. Other parameters that should be accounted for include the orientation of electric field lines and size of EDMEM stack i.e. ratio of electrode to membranes.

The present study, as part of a major research project funded by the German federal ministry of education and research, endeavors partly to characterize the performance of ion separation in an EDMEM under different geometrical and operating conditions. The paper begins with the introduction of objectives, then proceeds with the characterization of EDMEMs followed by the development of a new dimensionless number. To facilitate better insight, two case studies are also presented. Finally, challenges and further work are underlined and discussed.

2. Problem statement

Electrodialysis (ED) is a membrane process, in which salt ions are transported through semi-permeable membranes from one solution to another, e.g. from feed to concentrate, under the force of an electric potential gradient. The process is performed in a configuration called an ED cell which consists of feed and concentrate compartments. The cells are separated from each other by an AEM and a CEM. The whole configuration is placed between two electrodes as typically depicted in Fig. 1.

When an ion is subjected to an electric field $\vec{E}$, it moves naturally due to an electric force. The ion experiences this force at any spatial point relative to the electric source. The magnitude of this force depends on the extent of electric field and the charge

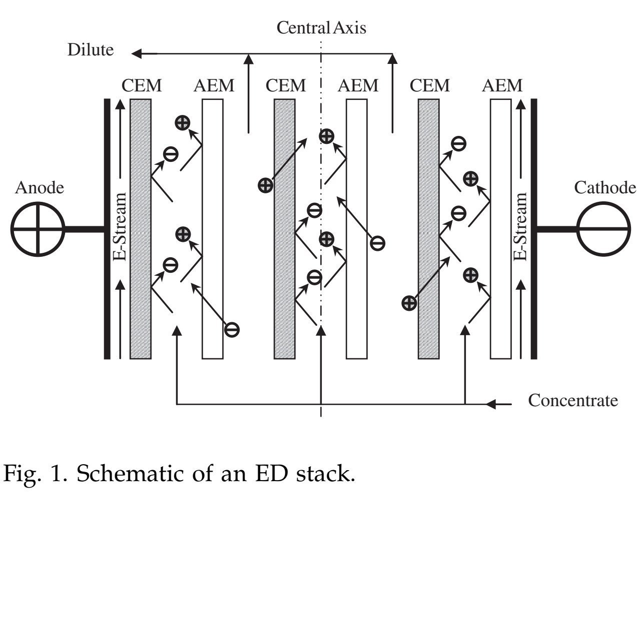

Fig. 1. Schematic of an ED stack.

density of ions. The direction of this movement nonetheless depends on the ion charge, i.e. anions move in the opposite direction of cations. The average velocity that an ion attains due to an electric field is termed as the *drift velocity* of any specific ion.

Referring to Fig. 1, in an EDMEM stack, the exerted electric field is not the sole driving force, which causes ions to move. In fact, the electrolytes which contain the ions, i.e. concentrate and dilute, flow with a characteristic velocity, which is considerably larger than the drift velocities of ions. For instance, in a typical small-size EDMEM stack in which the flow velocity of concentrate and dilute is about 4 cm/s and operates under an electric field with a magnitude equal to 4,000 V/m, the drift velocity of most ions is less than 0.15 cm/s.

In an EDMEM stack, the direction of the main flow stream of both compartments of dilute and concentrate is also the same. However, the overall electric field direction of EDMEM stack, which is characteristically from cathode to anode, is perpendicular to the main flow stream of both compartments of dilute and concentrate. When this happens at all spatial positions, then the force acting on each ion and the related drift velocity will also be perpendicular to the main flow direction of both dilute and concentrate compartment. Consequently, an effective diffusion and movement of ions form the dilute to concentrate compartment would take place.

Ion separation can be enhanced when the electric field lines tend to be perpendicular to the main flow streams at each spatial position. This can only be attained using enough large cathode and anode electrodes, which have the same wetted area as AEM and CEM. Nevertheless, in many commercial EDMEM stacks, the wetted area of electrodes is smaller to those of membranes. This is due to the operational problems, e.g. excessive heating of membranes. Accordingly, it is a common practice to place the electrodes concentrically to the membranes. In such a geometrical arrangement, the electric field lines and the main flow streams are not always perpendicular at each spatial position. Under such circumstances, it would be imperative to develop a model that would collectively contain as many as operating and geometrical parameters that would otherwise individually impact the performance of EDMEMs. This, nevertheless, would best be accomplished if such parameters are all integrated into a dimensionless number for rigorous appraisal of EDMEMs in terms of ion separation concerning the orientation of electric field lines with respect to the main flow streams. To do so, several assumptions need to be considered:

(1) The physical properties, e.g. viscosity and permittivity, are assumed to be homogeneous in the stack. This is despite the fact that in practice, the physical properties of AEM, CEM, dilute, and concentrate are different. Therefore, a specific ion behaves differently concerning its motion and transport rate when it passes through each component of the stack. The impact of otherwise feature i.e. heterogeneity is still a matter of further research but this assumption here is needed to facilitate the subsequent analysis.

(2) The dilute and concentrate are assumed to flow in parallel layers or simply move as plug flow. This, in practice, is not the case as commonly spacers are used in the flow channel of dilute and concentrate compartments, to keep, firstly, the two membranes apart; secondly, to enhance the mixing level in the direction of the flow and across the flow channel thickness, see Mohammadi and Malayeri [1,2] for more details. The latter would in turn decrease the thickness of the viscose boundary layer and accordingly enhance the overall performance of the EDMEM stack. Under such circumstances, the flow characteristic will be very complicated. For the sake of simplicity, the velocity of the fluid is assumed constant across the flow channel.

3. Development of a new dimensionless number, $H_E^{\bar{\beta}}$

Consider a uniform velocity vector $\vec{u}$ for a flowing electrolyte with a magnitude of $u(x,y) = u$. Simultaneously, an electric field $\vec{E}$ is exerted on this electrolyte at any arbitrary point (x,y), with a magnitude of $E(x,y) = E$. A schematic of these vector fields is illustrated in Fig. 2. The dash curves shown in Fig. 2, which are logically parallel to E_m, serve as electric field lines. Conventionally, the direction of $\vec{u}$ represents the positive direction of y axis and the direction of drift velocity $\vec{v}_d$ corresponds to the positive direction of x axis. Thus, in Fig. 2, the y component of $\vec{v}_d$ is in the same direction of $\vec{u}$. This condition can be presented mathematically as $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \geq 0$, and will be shown later with superscript $x \geq 0$.

Now, assume an ion at position (x,y) with a drift velocity of $\vec{v}_d$. It is then possible to define the ratio of vertical displacement of this ion, i.e. $d\mathcal{L}_y$ which is due to both fluid flow and the vertical component of its drift velocity, to its horizontal displacement, dx, which is only due to the horizontal component of its drift velocity at time interval dt:

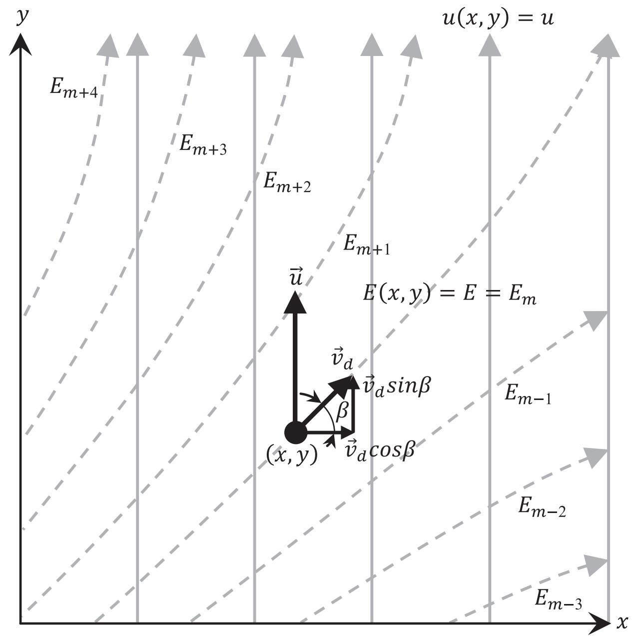

Fig. 2. The velocity vector field for a flowing electrolyte and the exerted electric field. The curve E_m represents the electric field lines.

$$\frac{d\mathcal{L}_y}{dx} = \frac{(|\vec{u}| + |\vec{v}_d| \sin\beta)dt}{(|\vec{v}_d| \cos\beta)dt} = \frac{|\vec{u}|}{|\vec{v}_d|}\sqrt{1+\tan^2\beta} + \tan\beta \tag{1}$$

Knowing that $\tan\beta$ represents the slope of curve $E(x,y) = E = E_m$ at position (x,y), then:

$$d\mathcal{L}_y = \frac{|\vec{u}|}{|\vec{v}_d|}\left(\sqrt{1+\left(\frac{dy}{dx}\bigg|_E\right)^2}\right)dx + \left(\frac{dy}{dx}\bigg|_E\right)dx \tag{2}$$

Integration of Eq. (2) for x interval $[0,\delta]$ then yields the overall vertical displacement of all ions located on curve $E(x,y) = E_m$ at time interval dt and for a characteristic length of δ, which is the distance between two membranes.

$$\Delta\mathcal{L}_y = \frac{|\vec{u}|}{|\vec{v}_d|}\mathcal{P}_E + \Delta y|_E \tag{3}$$

In Eq. (3), $\Delta\mathcal{L}_y$ is the overall vertical displacement of all ions located on curve $E(x,y)$ due to the flow and drift velocities of $\vec{u}$ and $\vec{v}_d$, $\mathcal{P}_E$ is the perimeter of curve $E(x,y)$, and $\Delta y|_E$, the vertical displacement of an ion, which moves only on curve $E(x,y)$. It is then possible to determine the overall displacement for all ions in electric field domain as:

$$\int \Delta\mathcal{L}_y dE = \int \frac{|\vec{u}|}{|\vec{v}_d|}\mathcal{P}_E dE + \int \Delta y|_E dE \quad (4)$$

Applying the integral averaging technique for Eq. (4) yields:

$$\frac{\overline{\Delta\mathcal{L}_y}}{\overline{\Delta y|_E}} = \frac{\frac{|\vec{u}|}{|\vec{v}_d|}\mathcal{A}_E}{\overline{\Delta y|_E E}} + 1 \quad (5)$$

In Eq. (5), $\mathcal{A}_E$ represents the overall surface of electric field profile $E = E(x, y)$. This can be defined as $\overline{\mathcal{P}_E}E$, where $\overline{\mathcal{P}_E}$ denotes a characteristic perimeter of electric field profile $E = E(x, y)$. Moreover, $\overline{\Delta\mathcal{L}_y}/\overline{\Delta y|_E}$ is the ratio of the average vertical displacement of ions affected by flow and electric fields to the average vertical displacement of ions affected only by electric field. Large $\overline{\Delta\mathcal{L}_y}/\overline{\Delta y|_E}$ indicates the movement of ions in the direction of main flow stream that is in vertical direction when the fluid flow is large, thus the ion separation is not appreciably effective. Contrariwise, small $\overline{\Delta\mathcal{L}_y}/\overline{\Delta y|_E}$ corresponds to a comparatively small vertical displacement of ion due to the fluid flow and, therefore, implies the efficiency (or even deficiency as will be discussed later) of ion separation. Now, we define $\overline{\Delta y|_E}/\overline{\Delta\mathcal{L}_y}$ as a new dimensionless number of $\mathbf{H}_\mathrm{E}$ (**H** is eta), which describes the quality of ion separation due to the relative orientation of flow and electric fields.

Referring to Eq. (5), dominator $\overline{\Delta y|_E E}$ has to meaningfully be defined. If the profile of electric field $E(x, y)$ is known, then the vertical displacement Δy can mathematically be related to the horizontal displacement Δx. Consequently, $\overline{\Delta y|_E E}$ can be described as $\overline{\tan\beta}\,\overline{\Delta x|_E}E$, where $\overline{\Delta x|_E}$ denotes the average horizontal displacement of an ion, which moves only on curve $E(x, y)$, and $\overline{\tan\beta}$ defines the average slope of curve $E(x, y)$. Now, consider that $\vec{E} = -\vec{\nabla}V$, and $\overline{\Delta x|_E E}$ represents the overall electric potential V applied to the stack. This would imply that instead of using $\overline{\Delta y|_E E}$ in Eq. (5), the overall electric potential V can be used. Moreover, if $|\vec{v}_d| = \kappa|\vec{E}|$, where κ is the ion mobility [3], then Eq. (5) can be rearranged in the following form:

$$\mathbf{H}_\mathrm{E}^{x\geq 0} = \frac{1}{1 + \frac{1}{\overline{\tan\beta}}\frac{u\overline{\mathcal{P}_E}}{\kappa V}} \quad (6)$$

Superscript $x \geq 0$ refers to the condition $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \geq 0$ that has been discussed before. Fig. 3 presents schematically the potential lines and electric field lines in a typical EDMEM stack, where condition $x \geq 0$ is valid for quadrants 2 and 4. However, in quadrants 1 and 3, the y component of $\vec{v}_d$ is in the opposite direction of $\vec{u}$. This can mathematically be represented as $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \leq 0$, which will be shown later with superscript $x \leq 0$. For quadrants of 1 and 3, applying the same method used for $\mathbf{H}_\mathrm{E}^{x\geq 0}$, then $\mathbf{H}_\mathrm{E}^{x\leq 0}$ becomes:

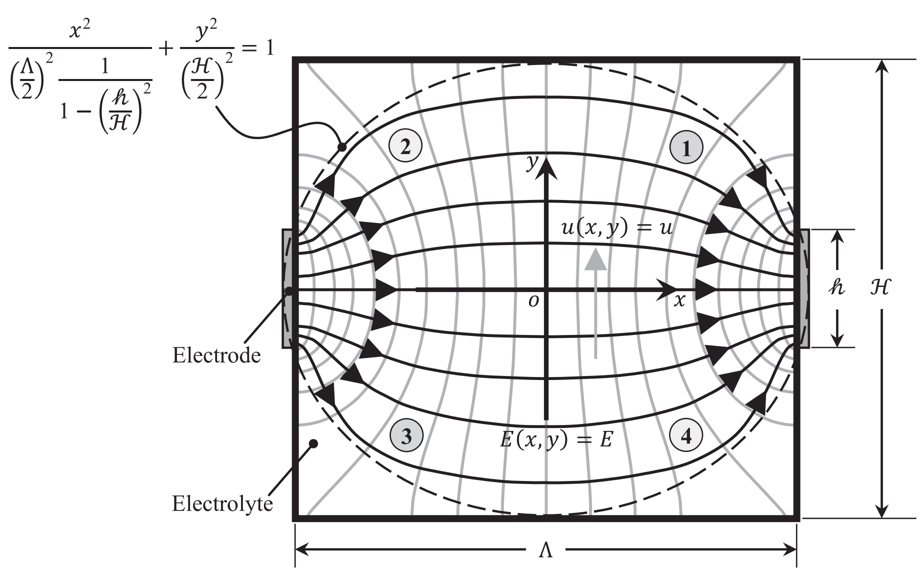

Fig. 3. Schematic of potential lines (grey) and electric field lines (black) in an EDMEM stack. The dashed ellipse represents the overall domain of effective electric field.

$$\mathbf{H}_{\mathrm{E}}^{\times \le 0} = \frac{1}{\left|1 - \frac{1}{\tan\beta}\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right|} \tag{7}$$

Having considered all directions of velocity and electric fields, now the overall value of $\mathbf{H}_{\mathrm{E}}$ should be deduced as a function of both $\mathbf{H}_{\mathrm{E}}^{\times \ge 0}$ and $\mathbf{H}_{\mathrm{E}}^{\times \le 0}$. When $u \ge \overline{\tan\beta}\kappa V/\overline{\mathcal{P}_E}$, the overall average vertical displacement of ions affected by flow and electric fields will be equal to the half of the summation of corresponding displacement obtained by $\mathbf{H}_{\mathrm{E}}^{\times \ge 0}$ and $\mathbf{H}_{\mathrm{E}}^{\times \le 0}$, i.e. $\overline{\Delta y|_E} = \left(\overline{\Delta y|_E^{\times \ge 0}} + \overline{\Delta y|_E^{\times \le 0}}\right)/2$. Hence, for $u \ge \overline{\tan\beta}\kappa V/\overline{\mathcal{P}_E}$, the value of $\mathbf{H}_{\mathrm{E}}$ will be $\mathbf{H}_{\mathrm{E}} = \left(\mathbf{H}_{\mathrm{E}}^{\times \ge 0} + \mathbf{H}_{\mathrm{E}}^{\times \le 0}\right)/2$. Similarly, but with a slight difference, when $u \le \overline{\tan\beta}\kappa V/\overline{\mathcal{P}_E}$, $\mathbf{H}_{\mathrm{E}}$ will be equal to the half of the summation of absolute values of corresponding displacement obtained by $\mathbf{H}_{\mathrm{E}}^{\times \ge 0}$ and $\mathbf{H}_{\mathrm{E}}^{\times \le 0}$, i.e. $\overline{\Delta y|_E} = \left(\left|\overline{\Delta y|_E^{\times \ge 0}}\right| + \left|\overline{\Delta y|_E^{\times \le 0}}\right|\right)/2$. Accordingly, if $u \le \overline{\tan\beta}\kappa V/\overline{\mathcal{P}_E}$, then $\mathbf{H}_{\mathrm{E}}$ will be $\mathbf{H}_{\mathrm{E}} = \left(\left|\mathbf{H}_{\mathrm{E}}^{\times \ge 0}\right| + \left|\mathbf{H}_{\mathrm{E}}^{\times \le 0}\right|\right)/2$. Hence, $\mathbf{H}_{\mathrm{E}}$ for all velocity domains will be defined as:

$$\mathbf{H}_{\mathrm{E}} = \frac{\left(\frac{1}{\tan\beta}\frac{u\overline{\mathcal{P}_E}}{\kappa V} - 1\right) H\left(\frac{1}{\tan\beta}\frac{u\overline{\mathcal{P}_E}}{\kappa V} - 1\right) + 1}{\left|\left(\frac{1}{\tan\beta}\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right)^2 - 1\right|} \tag{8}$$

where H is the Heaviside step function whose value is zero for negative and one for positive arguments. Although Eq. (8) defines $\mathbf{H}_{\mathrm{E}}$ as a function of operating conditions, still $\overline{\mathcal{P}_E}$ and $\overline{\tan\beta}$ are unknown.

In an EDMEM stack, each electric field line can be represented as a half of an ellipse, by applying topological isomorphism [4]. Thus, the area covered by electric field lines can be characterized by an ellipse. The semi-major and the semi-minor axes of this ellipse can be presented as the geometrical dimensions of the stack. Considering the Cartesian coordinate system presented in Fig. 3, the characteristic ellipse has a semi-major and a semi-minor axes equal to $(\Lambda/2)/\sqrt{1-(h/\mathcal{H})^2}$ and $\mathcal{H}/2$, respectively, where Λ is the distance between two electrodes or the width of stack, $\mathcal{H}$ is the height of stack, and h is the height of electrodes. The ratio of the perimeter of this ellipse to its semi-major axis, denoted as ψ, depends on its angular eccentricity and can indeed be considered as a measure of how much this ellipse deviates from being circular (or being rectangular). Using the Ramanujan's approximation for perimeter of an ellipse [5], ψ is then:

$$\psi = \pi\left\{3(1+\phi) - \sqrt{(3+\phi)(1+3\phi)}\right\} \tag{9}$$

where the aspect ratio ϕ is defined as:

$$\phi = \frac{\mathcal{H}}{\Lambda}\sqrt{1 - \left(\frac{h}{\mathcal{H}}\right)^2} \ge 0 \tag{10}$$

In domain of real numbers, Eq. (9) is a strictly increasing function since always $d\psi/d\phi \ge 0$. This is a very important property of ψ since it shows the minimum value of ψ will be obtained only when $\phi = 0$. Using Eqs. (9) and (10), $\overline{\mathcal{P}_E}$ for an EDMEM stack can be represented as:

$$\overline{\mathcal{P}_E} = \psi\frac{\Lambda}{4} \ge 0 \tag{11}$$

For stacks with very small electrodes and relatively equal width and height, i.e. $h/\mathcal{H} \to 0$ and $\mathcal{H} \cong \Lambda$, $\overline{\mathcal{P}_E}$ will be approximately equal to $\pi\Lambda/2$, which corresponds to the circumference of a semicircle of radius $\Lambda/2$. However, when the height of electrodes approaches the height of stack, that is, $h \to \mathcal{H}$, or when the width of stack becomes extremely long, i.e. $\Lambda \to \infty$, then $\overline{\mathcal{P}_E}$ becomes approximately equal to $\pi(3-\sqrt{3})\Lambda/4$. Importantly, when $h \to \mathcal{H}$ or when $\Lambda \to \infty$ the shape of ellipse becomes very similar to the shape of a rectangle, and at this condition, the value of $\overline{\mathcal{P}_E}$ asymptotes Λ. Interestingly, the deviation of $\pi(3-\sqrt{3})\Lambda/4$ from Λ is less than 0.42%, which shows the brilliant Ramanujan's approximation shown in Eq. (9).

For characterizing $\overline{\tan\beta}$, it is essential to find the order of magnitude of the orientation of electric field lines. The term $\overline{\tan\beta}$ describes the distinctive orientation of electric field lines with respect to the main flow stream. Fig. 4 presents the important geometrical aspects for characterization of $\overline{\tan\beta}$ (referring to Fig. 3, only quadrant 2 is depicted).

As it is schematically illustrated in Fig. 4, the overall paths of electric field can be mainly divided into two regions: right triangle ⊿**CBA** where the electric field lines are mostly inclined and rectangle □**CBDE**, where the electric field lines are orientated roughly horizontally. The characteristic orientation angle of electric field lines thus can be defined as the weighted mean of the characteristic angle of ⊿**CBA**, i.e. $\angle ABC = \overline{\beta}$, and the characteristic angle of □**CBDE**, that is zero since the electric field lines are supposed to be mostly horizontal. Considering the height of stack and electrode, the characteristic orientation angle

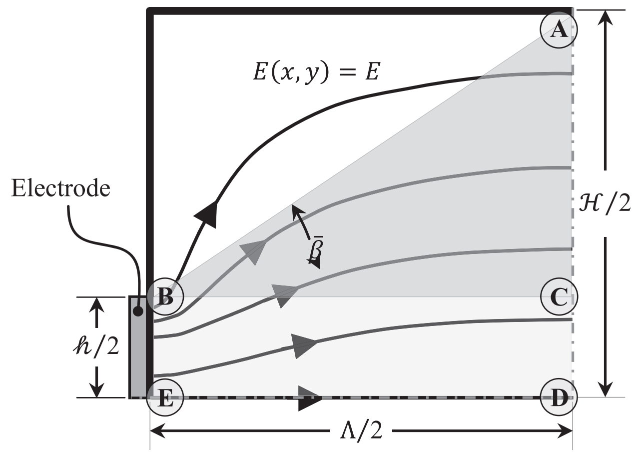

Fig. 4. Characterizing $\overline{\tan\beta}$, based on geometrical aspects of an EDMEM stack.

will then be equal to $\{(\overline{\beta})(\mathcal{H}/2 - h/2) + (0)(h/2)\}/(\mathcal{H}/2)$. Therefore, the characterization slope $\overline{\tan\beta}$ can be defined as:

$$\overline{\tan\beta} = \tan\left(\overline{\beta}\left(1 - \frac{h}{\mathcal{H}}\right)\right) = \tan\left(\frac{\Lambda}{\mathcal{H}}\overline{\beta}\tan\overline{\beta}\right)\bigg|\tan\overline{\beta} = \frac{\mathcal{H} - h}{\Lambda} \tag{12}$$

For very long stacks with short electrodes, i.e. $\mathcal{H} \gg h$, $\overline{\tan\beta} \approx \tan\overline{\beta} \approx \mathcal{H}/\Lambda$. However, for enough long electrodes, i.e. $\mathcal{H} \approx h$, $\overline{\tan\beta} \approx \tan\overline{\beta} \approx 0$ which shows that the electric field lines are orientated mostly horizontal, i.e. perpendicular to main flow stream.

Eqs. (8)–(12) simplify the new dimensionless number $\mathbf{H}_E$ as a function of operating conditions and geometrical aspects of EDMEM stack which can be used as a new criterion for interpretation of the ion separation effectiveness due to the relative orientation of flow and electric fields. The plot presented in Fig. 5 describes the behavior of dimensionless number $\mathbf{H}_E$ for an EDMEM stack with characteristic slope $\overline{\tan\beta} = 1$. Concerning Eq. (12), $\overline{\tan\beta} = 1$ may refer to an extreme condition in which the width of stack is equal to its height, i.e. $\Lambda = \mathcal{H}$, and the height of electrodes is much less than the height of stack, i.e. $h \lll \mathcal{H}$ or $h/\mathcal{H} \approx 0$.

For $u\overline{\mathcal{P}_E}/\kappa V = 0$, $\mathbf{H}_E$ is equal to 1. Knowing that the characteristic perimeter $\overline{\mathcal{P}_E}$ is not equal to zero, $u\overline{\mathcal{P}_E}/(\kappa V) = 0$ is valid only when $u \to 0$ or $\kappa \to \infty$ and also if $V \to \infty$. Under such circumstances, the force convective displacement of ions due to the fluid flow is much less than the displacement due to its drift

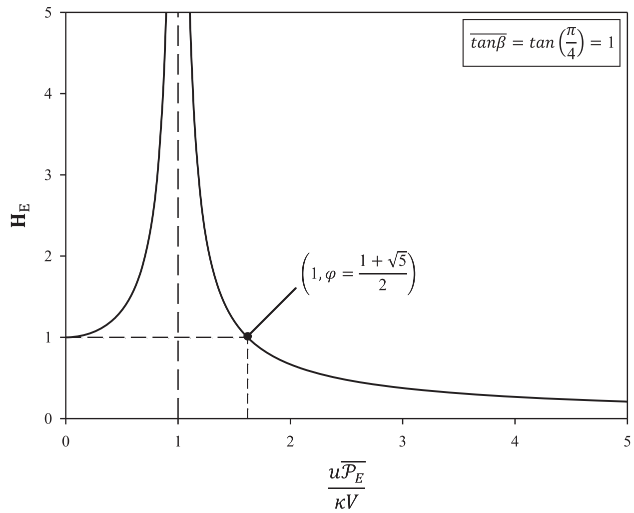

Fig. 5. $\mathbf{H}_E$ vs. $u\overline{\mathcal{P}_E}/(\kappa V)$ for an EDMEM stack with characteristic slope of $\overline{\tan\beta} = 1$.

velocity. Hence, the overall displacement of an ion is approximately equal to its displacement caused by electric field, which means $\mathbf{H}_E \to 1$ as is evidently shown in Fig. 5. In the meantime, $\mathbf{H}_E$ increases with $u\overline{\mathcal{P}_E}/(\kappa V)$ as long as $u\overline{\mathcal{P}_E}/(\kappa V) \leq 1$. This is an intriguing phenomenon, which can be attributed to the behavior of $\mathbf{H}_E$ in each individual quadrant depicted in Fig. 3. As a result, if $u\overline{\mathcal{P}_E} \to \kappa V$, then $\mathbf{H}_E^{\times \geq 0}$ in quadrants 2 and 4, where $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \geq 0$ approaches 1/2. This may decrease the value of $\mathbf{H}_E$ about 50%. However, in quadrants 1 and 3, where $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \leq 0$ the vertical component of $\vec{v}_d$, i.e. $\vec{v}_d \sin\beta$, is in the opposite direction of $\vec{u}$. Hence, lower ion mobility κ and/or dropping the voltage V would cause a reduction in the drift velocity $\vec{v}_d$. This in combination with higher $\vec{u}$ which in turn decreases the overall vertical displacement or increases the vertical residence time of ions in quadrants 1 and 3, which implies better performance of stack.

Interestingly, the integration of vertical displacement of an ion due to the drift velocity $\vec{v}_d$ will reduce by elongation of $\overline{\mathcal{P}_E}$. This is because as far as the characteristic perimeter $\overline{\mathcal{P}_E}$ increases, the orientation of electric field lines tend to be horizontal, i.e. perpendicular to velocity $\vec{u}$, and, therefore, the magnitude of vertical component of $\vec{v}_d$, i.e. $\vec{v}_d \sin\beta$, will be lower (see Fig. 3). Hence, for $u\overline{\mathcal{P}_E} \leq \kappa V$, increasing the value $u\overline{\mathcal{P}_E}/(\kappa V)$ will increase the value of $\mathbf{H}_E^{\times \leq 0}$. For example, increasing the value of $u\overline{\mathcal{P}_E}/(\kappa V)$ from 0 to 0.5 will reduce the value of $\mathbf{H}_E^{\times \geq 0}$ about 33.3%, and on the contrary, will increase $\mathbf{H}_E^{\times \leq 0}$ up to 100%. Thus, an average increase of about 33.3%, i.e. (100 − 33.3%)/2, would be expected for $\mathbf{H}_E$ (see Fig. 5).

For $u\overline{\mathcal{P}_E}/(\kappa V)\geq 1$, the convective term $u\overline{\mathcal{P}_E}$ is greater than the diffusive term κV. Hence, in all quadrants of an EDMEM stack (see Fig. 3), the vertical displacement of ions affected by flow and electric field will rise by increasing $u\overline{\mathcal{P}_E}$ and/or decreasing κV. Hence, increasing $u\overline{\mathcal{P}_E}$ and/or decreasing κV will reduce $\mathbf{H}_\mathrm{E}$. The reduction of $\mathbf{H}_\mathrm{E}$ can be obviously seen in Fig. 5 for $u\overline{\mathcal{P}_E}/(\kappa V)\geq 1$, which is an important observation.

The definition of $\mathbf{H}_\mathrm{E} = \overline{\Delta y|_E}/\overline{\Delta \mathcal{L}_y}$ can also be rewritten as $\overline{\Delta y|_E}/\left(\overline{\Delta y|_U}+\overline{\Delta y|_E}\right)$, where $\overline{\Delta y|_U}$ is the average vertical displacement of ions affected only by the flow. Now, $d\mathbf{H}_\mathrm{E} = \left(\overline{\Delta y|_U}d\overline{\Delta y|_E}-\overline{\Delta y|_E}d\overline{\Delta y|_U}\right)/\left(\overline{\Delta y|_U}+\overline{\Delta y|_E}\right)^2$, which defines the rate of change in $\mathbf{H}_\mathrm{E}$. This shows that the ascent in $\overline{\Delta y|_U}$ and the descent in $\overline{\Delta y|_E}$ will cause a negative growth rate of $\mathbf{H}_\mathrm{E}$. Quite the opposite, higher $\mathbf{H}_\mathrm{E}$ can be achieved by reducing $\overline{\Delta y|_U}$ and rising $\overline{\Delta y|_E}$. In the meantime, we know that the values of $\overline{\Delta y|_U}$ and $\overline{\Delta y|_E}$ can be altered only by changing $u\overline{\mathcal{P}_E}$ and κV, respectively, confirming that $\mathbf{H}_\mathrm{E}$ will reduce by increasing $u\overline{\mathcal{P}_E}/\kappa V$. For a certain EDMEM stack in which the electric field lines have a distinct orientation, i.e. $\overline{\beta}$ is constant, the ion convective motion is greater than the ion diffusive motion, i.e. $u\overline{\mathcal{P}_E}\geq\kappa V$. Then this occurs and $d\mathbf{H}_\mathrm{E}$ also shows that maximizing $\mathbf{H}_\mathrm{E}$ can be achieved only by reducing the vertical displacement due to the fluid flow, i.e. $\overline{\Delta y|_U}$. This can be accomplished by reducing $u\overline{\mathcal{P}_E}$ and/or by increasing the vertical displacement due to the electric field, i.e. $\overline{\Delta y|_E}$, which can be attained only by increasing κV. Therefore, in a certain EDMEM stack, where the profile of electric field lines is fixed, a greater value of $\mathbf{H}_\mathrm{E}$ is desired.

When $u\overline{\mathcal{P}_E}/(\kappa V)\geq 1$, and for a given $u\overline{\mathcal{P}_E}/(\kappa V)$, $\mathbf{H}_\mathrm{E}$ will have a value equivalent to the case where the flow velocity is equal to zero, i.e. where $\mathbf{H}_\mathrm{E}=1$. For an EDMEM stack with characteristic slope $\overline{\tan\beta}=1$, this occurs at $u\overline{\mathcal{P}_E}/\kappa V=\varphi$, where φ is the "Golden Ratio" equal to $\left(1+\sqrt{5}\right)/2$ (see Fig. 5). For $u\overline{\mathcal{P}_E}/(\kappa V)>\varphi$, $\mathbf{H}_\mathrm{E}<1$ and tends to zero. Therefore, for a certain EDMEM stack when the characteristic slope $\overline{\tan\beta}=1$, the desired value of $\mathbf{H}_\mathrm{E}$ will be obtained in the range of $0\leq u\overline{\mathcal{P}_E}/(\kappa V)\leq\varphi$. Referring to Eq. (8) for an EDMEM stack with characteristic slope $\overline{\tan\beta}$, the desired operating range will be $0\leq u\overline{\mathcal{P}_E}/(\kappa V)\leq\varphi\overline{\tan\beta}$. Importantly, for each value of $\mathbf{H}_\mathrm{E}$, where $\mathbf{H}_\mathrm{E}\geq 1$, two distinct values for $u\overline{\mathcal{P}_E}/\kappa V$ can be obtained: $u\overline{\mathcal{P}_E}/(\kappa V)=\overline{\tan\beta}\sqrt{1-1/\mathbf{H}_\mathrm{E}}$ and $u\overline{\mathcal{P}_E}/(\kappa V)=\overline{\tan\beta}\left(1+\sqrt{1+(2\mathbf{H}_\mathrm{E})^2}\right)/2\mathbf{H}_\mathrm{E}$.

The consumption of energy, i.e. lower voltage V, and higher production rate, i.e. increased fluid velocity u, is of prime importance for the operation of an efficient EDMEM stack. This can be obtained for a certain value of $\mathbf{H}_\mathrm{E}\geq 1$, when $u\overline{\mathcal{P}_E}/(\kappa V)=\overline{\tan\beta}\boldsymbol{\varphi}(\mathbf{H}_\mathrm{E})$. Here, function $\boldsymbol{\varphi}$ is defined as $\boldsymbol{\varphi}(x)=\left(1+\sqrt{1+(2x)^2}\right)/(2x)$, e.g. $\boldsymbol{\varphi}(1)=\varphi$. The desired range of $\mathbf{H}_\mathrm{E}$ is presented in Fig. 6 for an EDMEM stack with characteristic slope $\overline{\tan\beta}=1$.

Fig. 7 presents the behavior of $\mathbf{H}_\mathrm{E}$ for three EDMEM stacks of having arbitrary characteristic slopes of $\tan(\pi/8)$, $\tan(2\pi/8)$, and $\tan(3\pi/8)$, respectively. As the characteristic slope $\overline{\tan\beta}$ decreases, the curve of $\mathbf{H}_\mathrm{E}$ will be more narrow and less spread, sharper with propensity to move to the left.

For a certain value of $u\overline{\mathcal{P}_E}/(\kappa V)$, as the characteristic slope $\overline{\tan\beta}$ decreases, the electric field lines will tend to be orientated horizontally. Consequently, the average vertical displacement of ions affected only by electric field, i.e. $\overline{\Delta y|_E}$, will be reduced. This can be interpreted that when two different EDEME stacks at a definite value of $u\overline{\mathcal{P}_E}/(\kappa V)$ are compared, the stack which has a smaller value of $\mathbf{H}_\mathrm{E}$ will be preferred. In fact, at this condition, reducing the value of $\mathbf{H}_\mathrm{E}$ is not due to the magnification of convective term $u\overline{\mathcal{P}_E}$ and/or reduction of diffusion term κV, but is due to the declination of characteristic slope $\overline{\tan\beta}$. In other words, the orientation of electric field lines to the horizontal direction, i.e. perpendicular to the main flow stream, causes a reduction in $\mathbf{H}_\mathrm{E}$.

As for the characteristic orientation of electric field lines, two extreme cases should be considered for $\mathbf{H}_\mathrm{E}$:

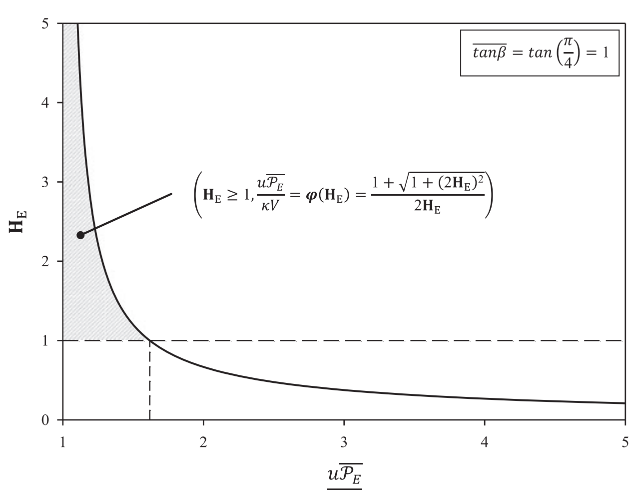

Fig. 6. Desired range of $\mathbf{H}_\mathrm{E}$ and $u\overline{\mathcal{P}_E}/(\kappa V)$ for an EDMEM stack with characteristic slope of $\overline{\tan\beta}=1$.

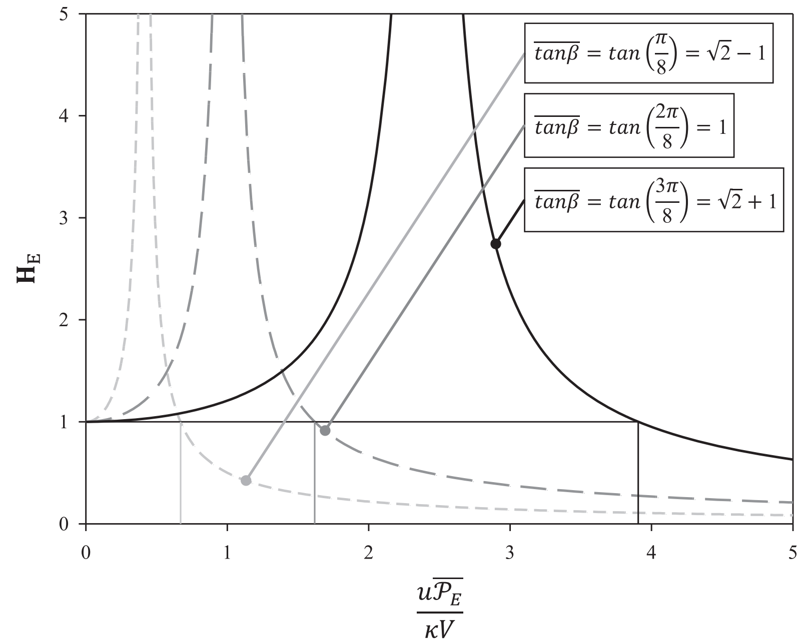

Fig. 7. $\mathbf{H}_{\mathrm{E}}$ vs. $u\overline{\mathcal{P}_E}/(\kappa V)$ for EDMEM stacks with different characteristic slopes of $\overline{\tan\beta}$.

first, when $\overline{\tan\beta} \to \tan(\pi/2)$ and second, when $\overline{\tan\beta} \to 0$. Referring to Eq. (12), for significantly long stacks with very small electrodes and narrow width, i.e. $\mathcal{H} \gg \Lambda \gg h$, $\overline{\tan\beta} \approx \tan\overline{\beta} \to \tan(\pi/2)$. This means that the electric field lines are orientated approximately vertically and they are nearly parallel to the main flow stream. Hence, knowing that $\overline{\tan\beta} \to \infty$, $\mathbf{H}_{\mathrm{E}}$ will be equal to one. This, however, does not mean that $\mathbf{H}_{\mathrm{E}}$ reaches the fairly desired value of one. Instead, it reflects the fact that there is no possibility to maximize $\mathbf{H}_{\mathrm{E}}$ since the electric field lines are parallel to the main flow stream. A quite distinctive condition is when the height of electrodes is equal to that of membranes, i.e. $\mathcal{H} = h$ and consequently $\overline{\tan\beta} \to 0$. To consider this scenario, it is essential to introduce a new special function $\mathcal{M}(a;x)$ which is defined as:

$$\mathcal{M}(a;x) = \left\{ \begin{array}{l} \mathcal{M}^{+}(a;x) = \begin{cases} a & x = 0 \\ 0 & x > 0 \end{cases} \\ \mathcal{M}^{-}(a;x) = \begin{cases} a & x = 0 \\ 0 & x < 0 \end{cases} \end{array} \right| \lim_{x\to 0^{+}} \mathcal{M}^{+}(a;x) = \lim_{x\to 0^{-}} \mathcal{M}^{-}(a;x) = +\infty \quad (13)$$

The function is very similar to Dirac delta when $a \to +\infty$, i.e. $\mathcal{M}(+\infty;x) \sim \delta(x)$. Nevertheless, $\mathcal{M}(+\infty;x)$ is not exactly equal to Dirac delta function since $\int_{-\infty}^{+\infty} \mathcal{M}(+\infty;x)dx \neq 1$. For an EDMEM stack with characteristic slope $\overline{\tan\beta} \to 0$, the behavior of $\mathbf{H}_{\mathrm{E}}$ can be described by $\mathcal{M}^{+}(1;x)$. At this condition, $\mathbf{H}_{\mathrm{E}} = 0$ for $x > 0$ indicates that the applied electric field makes no vertical displacement of ions since the electric field lines are orientated horizontally and are approximately perpendicular to the main flow stream. As $u\overline{\mathcal{P}_E}/(\kappa V)$ approaches an infinitesimal value greater than zero, i.e. $u\overline{\mathcal{P}_E}/(\kappa V) \to 0^{+}$, the ratio $(1/\overline{\tan\beta})u\overline{\mathcal{P}_E}/(\kappa V)$ tends to one. In other words, $(1/\overline{\tan\beta})u\overline{\mathcal{P}_E}/(\kappa V) \to 1^{+}$ thus one should expect that $\mathbf{H}_{\mathrm{E}} \to +\infty$. However, for a stagnant flow condition, where $u\overline{\mathcal{P}_E} = 0$, the value of $\mathbf{H}_{\mathrm{E}}$ is equal to one. This behavior of $\mathbf{H}_{\mathrm{E}}$, which can be described by the special function $\mathcal{M}^{+}(1;x)$, shows the best possible orientation of electric field lines.

As it has been explained, the complicated behavior of $\mathbf{H}_{\mathrm{E}}$ is due to different; and even counteracting effects of convective term $u\overline{\mathcal{P}_E}$, diffusive term κV, and orientation term $\overline{\tan\beta}$ which have to be considered simultaneously. Therefore, it is essential to modify the dimensionless number $\mathbf{H}_{\mathrm{E}}$ into a simpler and more meaningful form. For an EDMEM stack with characteristic slope $\overline{\tan\beta} = 1$, $\mathbf{H}_{\mathrm{E}}^{1}$ is defined as the dimensionless number $\mathbf{H}_{\mathrm{E}}$ for $u\overline{\mathcal{P}_E}/(\kappa V) \geq 1$:

$$\mathbf{H}_{\mathrm{E}}^{1} = \frac{\frac{u\overline{\mathcal{P}_E}}{\kappa V}}{\left(\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right)^{2} - 1} \quad (14)$$

Again, in Eq. (14), $u\overline{\mathcal{P}_E}/(\kappa V)$ has to be more than one. However, for $u\overline{\mathcal{P}_E}/(\kappa V)$ less than one, which will be referred with superscript ≤ 1, it is possible to calculate a corresponding value of $u\overline{\mathcal{P}_E}/(\kappa V)$, which is greater than one (see Fig. 6 and respective discussion). This corresponding value will be shown with superscript ≥ 1, thus:

$$\left(\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right)^{\geq 1} = \varsigma + \sqrt{1+\varsigma^2}\Bigg|\varsigma = \frac{1-\left(\left(\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right)^{\leq 1}\right)^2}{2} \tag{15}$$

Now, if one considers Eqs. (14) and (15), then the modified dimensionless number $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ for an EDMEM stack with characteristic slope $\overline{\tan\beta}$ can be written as:

$$\mathbf{H}_\mathrm{E}^{\bar{\beta}} = \frac{\mathbf{H}_\mathrm{E}^1}{\overline{\tan\beta}} = \frac{1}{\overline{\tan\beta}} \frac{\left(\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right)^{\geq 1}}{\left(\left(\frac{u\overline{\mathcal{P}_E}}{\kappa V}\right)^{\geq 1}\right)^2 - 1} \tag{16}$$

The desired range for $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ and $(u\overline{\mathcal{P}_E}/\kappa V)^{\geq 1}$ can now be defined as the range where $\mathbf{H}_\mathrm{E}^{\bar{\beta}} \geq 1$. As a result, the desired value of $(u\overline{\mathcal{P}_E}/\kappa V)^{\geq 1}$ will be $1 \leq (u\overline{\mathcal{P}_E}/\kappa V)^{\geq 1} \leq \boldsymbol{\varphi}\left(\overline{\tan\beta}\mathbf{H}_\mathrm{E}^{\bar{\beta}}\right)$ (see also Figs. 5 and 6 and respective discussion). Fig. 8 represents the dimensionless number $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ as a function of $(u\overline{\mathcal{P}_E}/\kappa V)^{\geq 1}$ and characteristic slope $\overline{\tan\beta}$ for an EDMEM stack. It is evident that lowering the characteristic slope $\overline{\tan\beta}$ will spread the range of the desired value of $(u\overline{\mathcal{P}_E}/\kappa V)^{\geq 1}$.

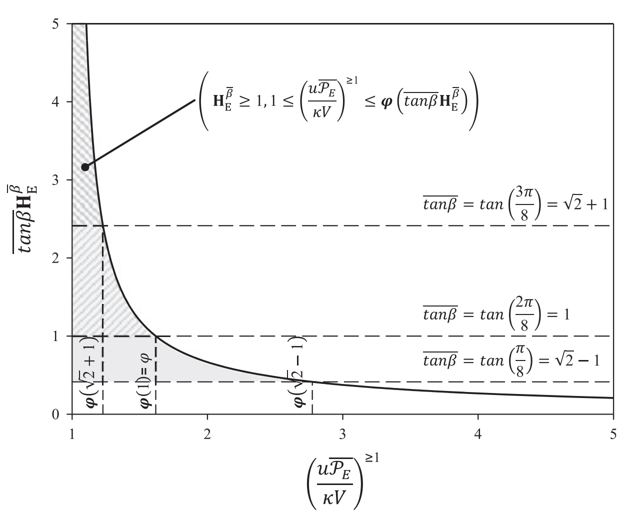

Fig. 8. $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ vs. $\left(u\overline{\mathcal{P}_E}/\kappa V\right)^{\geq 1}$ for an EDMEM stack with characteristic slope of $\overline{\tan\beta}$.

The new modified dimensionless number $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ characterizes the effectiveness of ion separation by considering (1) the orientation of electric field lines with respect to the main flow stream direction, (2) the convective term $u\overline{\mathcal{P}_E}$, and (3) the diffusive term κV. It can also facilitate to find out the efficient operating conditions when $\mathbf{H}_\mathrm{E}^{\bar{\beta}} \geq 1$. Moreover, it can improve the performance of an EDMEM stack by tuning the dimensionless parameter $u\overline{\mathcal{P}_E}/(\kappa V)$ to $(u\overline{\mathcal{P}_E}/\kappa V)^{\geq 1}$, when $u\overline{\mathcal{P}_E}/(\kappa V) \leq 1$. For $u\overline{\mathcal{P}_E}/(\kappa V) \geq 1$, $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ shows that an effective ion separation can be achieved by:

- lower fluid velocity, u;
- lower $\overline{\mathcal{P}_E}$, e.g. the distance between two electrodes;
- lower characteristic slope, $\overline{\tan\beta}$;
- higher ion mobility, κ; and also
- higher overall stack voltage V.

4. $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ and Péclet number

The drift velocity, v_d, can be formulated as $v_d = -\kappa\partial V/\partial x$. In mass transfer, under steady state conditions, the Fick's law relates the diffusive flux to the concentration as $J = -D\partial\Phi/\partial x$, where J is the diffusion flux, D is the diffusion coefficient or the diffusivity, and Φ is the concentration for ideal mixtures. An analogy between these two equations shows that mobility κ can be related to diffusivity D. In gases, for instance, κ and D can be connected linearly to each other using Einstein–Smoluchowski relation as $D = \kappa k_B T/q$, where q is the electrical charge of ion and k_B is the Boltzmann constant [6,7]. Furthermore, the mass transfer diffusivity D is similar to the thermal diffusivity α. Hence, the product κV has the similar physical interpretation as diffusivity D and α. This implies that the dimensionless parameter $u\overline{\mathcal{P}_E}/(\kappa V)$ is indeed similar to the Péclet number, Pe, in heat and mass transfer. Therefore, $\mathbf{H}_\mathrm{E}^{\bar{\beta}}$ can be rearranged in a better conventional engineering form as:

$$\overline{\tan\beta}\,\mathbf{H}_\mathrm{E}^{\bar{\beta}} = \frac{Pe_\kappa^{\geq 1}}{\left(Pe_\kappa^{\geq 1}\right)^2 - 1} \tag{17}$$

In Eq. (17), subscript κ emphasizes that the diffusion term of Péclet number is defined as product of κV. Moreover, superscript ≥1 asserts that the Péclet number has to be greater than one. For enough large Péclet numbers, i.e. $Pe_\kappa \geq 5$, $(Pe_\kappa)^2 - 1$ is approximately equal to $(Pe_\kappa)^2$ with a relative error less than 4%. Thus, applying superscript ≥5 for emphasizing that the Péclet number has to be greater than five, Eq. (17) will be simplify to:

$$\overline{\tan\beta}\,\mathbf{H}_{\mathrm{E}}^{\overline{\beta}} = \frac{1}{Pe_{\kappa}^{\geq 5}} \tag{18}$$

5. Flowchart and case studies

The proposed dimensionless number of $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$ can be used for comparing the separation performance of different stacks, as well as for the design purposes under assumptions made in the preceding sections. The latter means, for a preferred value of $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$, it is possible to do a back calculation and find the desired design parameters. If one considers that the degree of freedom of $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$ is six, i.e. $\mathcal{N}_{\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}(h,\mathcal{H},\Lambda,u,\kappa,V)} = 6$, when five of the independent parameters are known, then it is possible to calculate the design parameter of interest when $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$ is known. The flowchart presented in Fig. 9, nevertheless, summarizes the forward calculation of $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$.

In order to have an engineering sense of the practical application of $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$, two case studies are provided. The cases are based on Electrodialysis Cell Unit ED 64 0 02 made by PCCell GmbH [8].

Case study 1:
An EDMEM stack consists of 25 cell pairs. The cell thickness is 0.5 mm and the cross-sectional flow area in each cell pair is 40 mm^2. The effective height of stack is 80 mm and the height of electrodes is 60 mm. The voltage difference at each cell pair is 2 V. The cell is considered for the purification of water by removing ions having ion mobility in the range of $6.98 \times 10^{-8}\mathrm{m}^2/(\mathrm{sV}) \leq \kappa \leq 8.10 \times 10^{-8}\mathrm{m}^2/(\mathrm{sV})$. The question is to find out the minimum fluid flow velocity required to have an optimum ion separation.

Solution:
The overall voltage is 25 (cell pairs) × 2 (V/cell pair) = 50 V, and Λ will be equal to 25 (cell pairs) × 0.5 mm (cell thickness) = 12.5 mm. $\mathcal{H}$ and h are also 80 and 60 mm, respectively.

Step 1: calculation of $\overline{\mathcal{P}}_E$
Using Eq. (10), ϕ will be equal to:

$$\phi = \frac{\mathcal{H}}{\Lambda}\sqrt{1-\left(\frac{h}{\mathcal{H}}\right)^2} = \frac{80\,\mathrm{mm}}{12.5\,\mathrm{mm}}\sqrt{1-\left(\frac{60\,\mathrm{mm}}{80\,\mathrm{mm}}\right)^2} = 4.23$$

Applying Eq. (9), ψ is then:

$$\psi = \pi\left\{3(1+\phi) - \sqrt{(3+\phi)(1+3\phi)}\right\}$$
$$= \pi\left\{3(1+4.23) - \sqrt{(3+4.23)(1+3\times 4.23)}\right\} = 18.05$$

Now, concerning Eq. (11), $\overline{\mathcal{P}}_E$ will be:

$$\overline{\mathcal{P}}_E = \psi\frac{\Lambda}{4} = 18.05 \times \frac{12.5\,\mathrm{mm}}{4} = 56.4\,\mathrm{mm}$$

Step 2: Calculation of characteristic slope $\overline{\tan\beta}$
Using Eq. (12), $\tan\overline{\beta}$, $\overline{\beta}$, and finally $\overline{\tan\beta}$ can be obtained as:

$$\tan\overline{\beta} = \frac{\mathcal{H}-h}{\Lambda} = \frac{80\,\mathrm{mm} - 60\,\mathrm{mm}}{12.5\,\mathrm{mm}} = 1.6$$

$$\overline{\beta} = Arc\tan(\tan\overline{\beta}) = Arc\tan(1.6) = 1.0122$$

$$\overline{\tan\beta} = \tan\left(\overline{\beta}\left(1-\frac{h}{\mathcal{H}}\right)\right) = \tan\left(\frac{12.5\,\mathrm{mm}}{80\,\mathrm{mm}}1.6\times 1.0122\right)$$
$$= 0.2586$$

Step 3: calculation of $\boldsymbol{\varphi}\left(\overline{\tan\beta}\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}\right)$

Knowing that $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$ should be greater or equal to one, if $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}} = 1$, then $\boldsymbol{\varphi}\left(\overline{\tan\beta}\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}\right)$ is equal to $\boldsymbol{\varphi}\left(\overline{\tan\beta}\right)$:

$$\boldsymbol{\varphi}\left(\overline{\tan\beta}\right) = \frac{\left(1+\sqrt{1+\left(2\overline{\tan\beta}\right)^2}\right)}{2\overline{\tan\beta}}$$
$$= \frac{\left(1+\sqrt{1+(2\times 0.2586)^2}\right)}{2\times 0.2586} = 4.1104$$

Step 4: Calculation of flow velocity

The velocity range will be $\kappa V/\overline{\mathcal{P}_{\mathcal{E}}} \leq u \leq \boldsymbol{\varphi}\left(\overline{\tan\beta}\right)\kappa V/\overline{\mathcal{P}}_E$, since $1 \leq u\overline{\mathcal{P}_E}/\kappa V \leq \boldsymbol{\varphi}\left(\overline{\tan\beta}\right)$.

For minimum ion mobility, i.e. $\kappa = 6.98 \times 10^{-8} m^2/(sV)$:

$$\frac{\kappa V}{\overline{\mathcal{P}_{\mathcal{E}}}} = \frac{6.98\times 10^{-8}\,\frac{\mathrm{m}^2}{\mathrm{s\cdot V}}\times 50\,\mathrm{V}}{56.4\,\mathrm{mm}\times\frac{1\,\mathrm{m}}{1{,}000\,\mathrm{mm}}} = 6.2\times 10^{-5}\,\frac{\mathrm{m}}{\mathrm{s}} = 0.0062\,\frac{\mathrm{cm}}{\mathrm{s}}$$

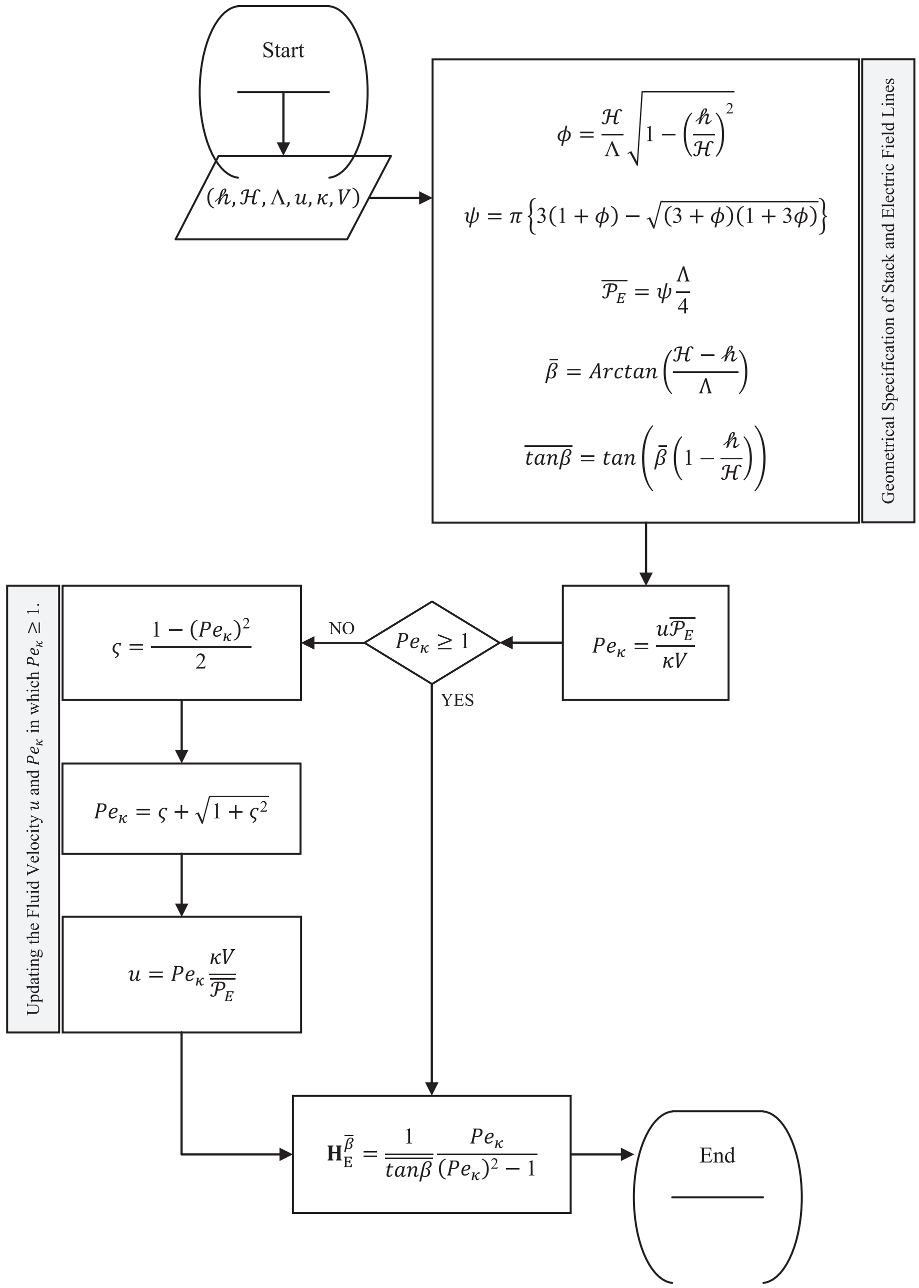

Fig. 9. Flowchart for forward calculation of $H_E^{\bar{\beta}}$.

$$\varphi\left(\overline{\tan\beta}\right)\frac{\kappa V}{\overline{\mathcal{P}_E}} = 4.1104 \times 0.0062\,\frac{\text{cm}}{\text{s}} = 0.0254\,\frac{\text{cm}}{\text{s}}$$

$$0.0062\,\frac{\text{cm}}{\text{s}} \leq u \leq 0.0254\,\frac{\text{cm}}{\text{s}}$$

For maximum ion mobility, i.e. $\kappa = 8.10\times\ 10^{-8}\text{m}^2/(\text{s V})$:

$$\frac{\kappa V}{\overline{\mathcal{P}_\mathcal{E}}} = \frac{8.10 \times 10^{-8}\,\frac{\text{m}^2}{\text{s V}} \times 50\,\text{V}}{56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}} = 7.2 \times 10^{-5}\,\frac{\text{m}}{\text{s}} = 0.0072\,\frac{\text{cm}}{\text{s}}$$

$$\varphi\left(\overline{\tan\beta}\right)\frac{\kappa V}{\overline{\mathcal{P}_\mathcal{E}}} = 4.1104 \times 0.0072\,\frac{\text{cm}}{\text{s}} = 0.0295\,\frac{\text{cm}}{\text{s}}$$

$$0.0072\,\frac{\text{cm}}{\text{s}} \leq u \leq 0.0295\,\frac{\text{cm}}{\text{s}}$$

The range of inlet velocity is now obtained; however, it is essential to ensure that $Pe_\kappa \geq 1$ for all possible velocity ranges.

Step 5: re-calculation of Pe_κ
For velocity range $0.0072\,\text{cm/s} \leq u \leq 0.0295\,\text{cm/s}$ and $\kappa = 6.98 \times 10^{-8}\,\text{m}^2/(\text{sV})$:

$$u = 0.0072\frac{\text{cm}}{\text{s}} : Pe_\kappa = \frac{u\overline{\mathcal{P}\varepsilon}}{\kappa V} = \frac{7.2\times10^{-5}\,\frac{\text{m}}{\text{s}} \times 56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}}{6.98\times10^{-8}\,\frac{\text{m}^2}{\text{sV}} \times 50\,\text{V}} = 1.16 \geq 1$$

$$u = 0.0295\frac{\text{cm}}{\text{s}} : Pe_\kappa = \frac{u\overline{\mathcal{P}\varepsilon}}{\kappa V} = \frac{2.95\times10^{-4}\,\frac{\text{m}}{\text{s}} \times 56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}}{6.98\times10^{-8}\,\frac{\text{m}^2}{\text{s V}} \times 50\,\text{V}} = 4.77 \geq 1$$

For velocity range $0.0062\,\text{cm/s} \leq u \leq 0.0254\,\text{cm/s}$ and $\kappa = 8.10 \times 10^{-8}\,\text{m}^2/(\text{sV})$:

$$u = 0.0062\frac{\text{cm}}{\text{s}} : Pe_\kappa = \frac{u\overline{\mathcal{P}\varepsilon}}{\kappa V} = \frac{6.2\times10^{-5}\,\frac{\text{m}}{\text{s}} \times 56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}}{8.10\times10^{-8}\,\frac{\text{m}^2}{\text{sV}} \times 50\,\text{V}} = 0.86 < 1$$

$$u = 0.0254\frac{\text{cm}}{\text{s}} : Pe_\kappa = \frac{u\overline{\mathcal{P}\varepsilon}}{\kappa V} = \frac{2.54\times10^{-4}\,\frac{\text{m}}{\text{s}} \times 56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}}{8.10\times10^{-8}\,\frac{\text{m}^2}{\text{sV}} \times 50\,\text{V}} = 3.54 \geq 1$$

Re-calculation of Pe_κ shows that only for velocity $u = 0.0062\,\text{cm/s}$ and ion mobility $\kappa = 8.10\times 10^{-8}\text{m}^2/(\text{sV})$, the value of Pe_κ is less than 1. In order to maximize the production rate of this particular EDMEM stack, the largest calculated velocity should be considered. Therefore, the minimum desired inlet velocity is $u = 0.0295\,\text{cm/s}$.

Case study 2:
Consider that the EDMEM stack detailed in case study 1 operates with two nominal volumetric flow rates of 4 and 8 l/h for each cell pairs. Moreover, the voltage difference at each cell pair is 3 V. If the average ion mobility is equal to $7.54 \times 10^{-8}\,\text{m}^2/(\text{sV})$, then calculate $\mathbf{H}_\text{E}^{\bar{\beta}}$ for the above-mentioned flow rates.

Solution:
The overall voltage is 25 (cell pairs) × 3 (V/cell pair) = 75 V. The corresponding inlet velocities are:

$$4\frac{\text{l}}{\text{h}} : u = \frac{4\,\frac{\text{l}}{\text{h}} \times \frac{1\,\text{m}^3}{1{,}0001} \times \frac{1\,\text{h}}{3{,}600\,\text{s}}}{40\,\text{mm}^2 \times \left(\frac{1\,\text{m}}{1{,}000\,\text{mm}}\right)^2} = 0.0278\frac{\text{m}}{\text{s}} = 2.78\frac{\text{cm}}{\text{s}}$$

$$8\frac{\text{l}}{\text{h}} : u = \frac{8\,\frac{\text{l}}{\text{h}} \times \frac{1\,\text{m}^3}{1{,}0001} \times \frac{1\,\text{h}}{3{,}600\,\text{s}}}{40\,\text{mm}^2 \times \left(\frac{1\,\text{m}}{1{,}000\,\text{mm}}\right)^2} = 0.056\frac{\text{m}}{\text{s}} = 5.56\frac{\text{cm}}{\text{s}}$$

Step 1: calculation of Pe_κ

$$u = 2.78\frac{\text{cm}}{\text{s}} : Pe_\kappa = \frac{u\overline{\mathcal{P}\varepsilon}}{\kappa V} = \frac{0.0278\,\frac{\text{m}}{\text{s}} \times 56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}}{7.54\times10^{-8}\,\frac{\text{m}^2}{\text{s V}} \times 75\,\text{V}} = 277.26 \geq 1$$

$$u = 5.56\frac{\text{cm}}{\text{s}} : Pe_\kappa = \frac{u\overline{\mathcal{P}\varepsilon}}{\kappa V} = \frac{0.0556\,\frac{\text{m}}{\text{s}} \times 56.4\,\text{mm} \times \frac{1\,\text{m}}{1{,}000\,\text{mm}}}{7.54\times10^{-8}\,\frac{\text{m}^2}{\text{s V}} \times 75\,\text{V}} = 554.52 \geq 1$$

Step 2: calculation of $\mathbf{H}_\text{E}^{\bar{\beta}}$
Using Eq. (18):

$$u = 2.78\frac{\text{cm}}{\text{s}} : \mathbf{H}_\text{E}^{\bar{\beta}} = \frac{1}{\overline{\tan\beta}}\frac{1}{Pe_\kappa^{\geq 5}} = \frac{1}{0.2586}\frac{1}{277.26} = 0.014$$

$$u = 5.56\frac{\text{cm}}{\text{s}} : \mathbf{H}_\text{E}^{\bar{\beta}} = \frac{1}{\overline{\tan\beta}}\frac{1}{Pe_\kappa^{\geq 5}} = \frac{1}{0.2586}\frac{1}{554.52} = 0.007$$

The results show that the calculated value of $\mathbf{H}_\text{E}^{\bar{\beta}}$ for volumetric flow rate 4 l/h is two times greater than the corresponding value for 8 l/h. Therefore, for this stack, it is desired to operate at volumetric flow rate 4 l/h.

6. Challenges and future work

In spite of the above promising results, formidable challenges still lay ahead, which must be addressed through rigorous further theoretical and experimental studies. This is because the analysis presented in this study is obtained on the assumptions that: firstly, the physical properties of all components of the stack are homogeneous and constant which, for instance, do not change with time; and secondly, the flow is plug. The assumptions facilitated the development of the model that can help engineers, as an approximate tool, to assess the impact of geometrical aspect of the stack and operating conditions on the performance of ion separation. Nevertheless, these can hardly be relied upon in reality because of non-homogeneity in physical properties and also the effect of spacer in flow profile and mixing enhancement. For instance, the conductivity and permittivity of an electrolyte increases with its salt concentration. An electrolyte with higher salinity supports the formation of electric field better than the same electrolyte but with lower salinity. Hence, the behavior of concentrate compartment in formation of electric field is different that of dilute.

Furthermore, one should also note that physical properties of stack components including membranes and compartments may be time dependent. For instance, in the course of operation, the ion concentration increases in concentrate compartment and, consequently, its permittivity increases, which subsequently may influence the profile of electric field. In addition, the impact of other detrimental phenomena, e.g. concentration polarization and fouling, on separation performance of EDMEM stack has to rigorously be investigated.

7. Concluding remarks

The performance of an EDMEM stack in terms of ion separation is parameterized as a function of a new dimensionless number $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$. It characterizes the ion separation as a function of: (1) both operating conditions and geometry of stack in terms of Péclet number, $Pe_{\kappa} = u\overline{\mathcal{P}_E}/(\kappa V)$; and (2) the orientation of electric field lines with respect to the main flow stream, which can be represented by characteristic slope $\overline{\tan\beta}$. When the electric field lines are parallel to the main flow stream, for instance, the separation of ions reaches its minimum possible value. Contrariwise, the separation will be maximized when the electric field lines are perpendicular to the flow direction of main stream. Nevertheless, the enhancement of the separation process in an EDMEM stack depends also on some other fundamental physical properties of ions like the ion mobility, as it is presented in terms of the Péclet number Pe_{κ}. For ions with large mobility, an EDMEM stack can operate under relatively high flow velocity. However, for ion with low mobility, one should reduce the volumetric flow rate, which can be achieved by reducing the flow velocity or characteristic perimeter of stack, i.e. $\overline{\mathcal{P}_E}$. Finally, $\mathbf{H}_{\mathrm{E}}^{\overline{\beta}}$ can be used as a design tool for engineers in order to compare different EDMEM stacks and/or to optimize the operating conditions as well as stack dimensions.

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Nomenclature

D	—	mass transfer diffusion coefficient or diffusivity, m^2/s
E	—	electric field, V/m
h	—	height of electrodes, m
$\mathcal{H}$	—	height of stack, m
J	—	mass transfer diffusion flux, $mol/(m^2\,s)$
k_B	—	Boltzmann constant, $1.380648813 \times 10^{23}$ J/K
$\mathcal{N}$	—	degree of freedom, −
q	—	electrical charge of ion, C
t	—	time, s
T	—	absolute temperature, K
u	—	fluid velocity, m/s
v_d	—	drift velocity, m/s
V	—	electric potential, V
x	—	any point on x axis of Cartesian coordinates system, m
y	—	any point on y axis of Cartesian coordinates system, m

Greek symbols

α	—	thermal diffusivity, m^2/s
β	—	local angular orientation of electric field lines, rad
$\overline{\beta}$	—	corresponds to characteristic orientation angle of electric field lines, rad
δ	—	characteristic length, m
Δ	—	overall difference or change of a parameter, −
κ	—	ion mobility, $m^2/(s\,V)$
Λ	—	distance between two electrodes or the width of stack, m
Φ	—	concentration, mol/m^3

Mathematical symbols, operators, and special notations

$\overline{\ }$	—	characteristic value or average value
$[,]$	—	closed interval: $[a, b]$ or $a \le x \le b$
$\vec{\nabla}$	—	del gradient operator
$\mathcal{A}_E$	—	overall surface of electric field profile E defined as $\overline{\mathcal{P}_E}E$, Vm/m
$\mathcal{L}_y$	—	vertical displacement of ion, m

$\mathcal{M}(a;x)$ — new special function defined in Eq. (13)
$\mathcal{P}_E$ — perimeter of an electric field line E which is presented by geometrical function $E(x, y)$ in a two dimensional Cartesian coordinates system, m
$\overline{\tan\beta}$ — characteristic slope of electric field E which describes the distinctive orientation of electric field lines with respect to the main flow stream, −
$\delta(x)$ — Dirac delta function

Subscripts

E — refers to electric field
U — refers to the average vertical displacement of ions affected only by the flow

Superscripts

− — refers to a mathematical condition where the argument of a function is less than or equal to 0
\+ — refers to a mathematical condition where the argument of a function is greater than or equal to 0
$x \le 0$ — related to the condition where $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \le 0$
$x \ge 0$ — related to the condition where $|\vec{v}_d \times \vec{u}|/(|\vec{v}_d| \cdot |\vec{u}|) \ge 0$
≤ 1 — mathematical condition where the corresponding argument is less than or equal to 1
≥ 1 — mathematical condition where the corresponding argument is greater than or equal to 1
≥ 5 — mathematical condition where the corresponding argument is greater than or equal to 5

Dimensionless numbers

Pe_κ — Péclet number based on ion mobility κ defined as $u\overline{\mathcal{P}_E}/\kappa V$
$\mathbf{H}_\mathrm{E}$ — describes the ion separation due to the relative orientation of flow and electric fields (**H** is the uppercase of Greek symbol η; eta)
$\mathbf{H}_\mathrm{E}^1$ — dimensionless number $\mathbf{H}_\mathrm{E}$ for $u\overline{\mathcal{P}_E}/(\kappa V) \ge 1$
$\mathbf{H}_\mathrm{E}^{\overline{\beta}}$ — modified dimensionless number defined as $\mathbf{H}_\mathrm{E}^{\overline{\beta}} = \mathbf{H}_\mathrm{E}^1/\overline{\tan\beta}$
ς — dimensionless number equal to $\left(1-(Pe_\kappa)^2\right)/2$
φ — aspect ratio of characteristic ellipse of an EDMEM stack
ϕ — "Golden Ratio" equal to $\left(1+\sqrt{5}\right)/2$
$\boldsymbol{\varphi}(x)$ — dimensionless function defined as $\boldsymbol{\varphi}(x) = \left(1+\sqrt{1+(2x)^2}\right)/(2x)$, where the argument x is dimensionless. For $x = 1$, $\boldsymbol{\varphi}$ is equal to "Golden Ratio", i.e. $\boldsymbol{\varphi}(1) = \varphi$
ψ — dimensionless perimeter of an ellipse as a function of ellipse aspect ratio ϕ based on Ramanujan's approximation formula

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