Determination of limiting current density and current efficiency in electrodialysis units

Mariagiorgia La Cerva[a], Luigi Gurreri[a,*], Michele Tedesco[b], Andrea Cipollina[a], Michele Ciofalo[a], Alessandro Tamburini[a], Giorgio Micale[a]

[a] Dipartimento dell'Innovazione Industriale e Digitale (DIID), Università degli Studi di Palermo (UNIPA), viale delle Scienze Ed. 6, 90128 Palermo, Italy
[b] Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911, MA, Leeuwarden, the Netherlands

GRAPHICAL ABSTRACT
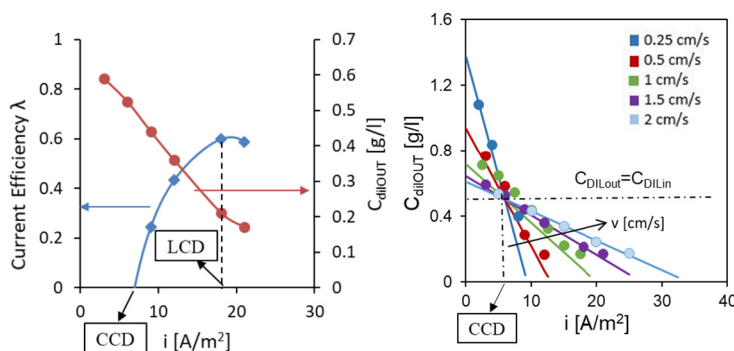
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ABSTRACT

A crucial parameter for the design and operation of electrodialysis (ED) units is the limiting current density (LCD). This is often identified with the diffusion-limited current density, which corresponds to the complete solute depletion in the layer adjacent to the membrane. Current-voltage curves obtained from measurements with electrodes in contact with the solution (i.e. without membranes) are consistent with this interpretation and exhibit a horizontal plateau identifying LCD. However, real ED systems show more complex behaviours, with a reduced-slope tract instead of a plateau and a third region in which the current increases more markedly (overlimiting current). The phenomena involved in the limiting region are not yet totally characterized and the determination of LCD in ED units is still ambiguous. In the present work, we explore the issues related to the identification of LCD, by measurements on ED units, assessing the influence of operating conditions and validating a simplified process simulator. A new method to determine LCD, based on the current efficiency, is proposed and compared with other methods presented in the literature. A second limiting quantity is also identified, i.e. the critical current density, below which diffusion phenomena prevail on migration and a method for its assessment is proposed.

* Corresponding author.
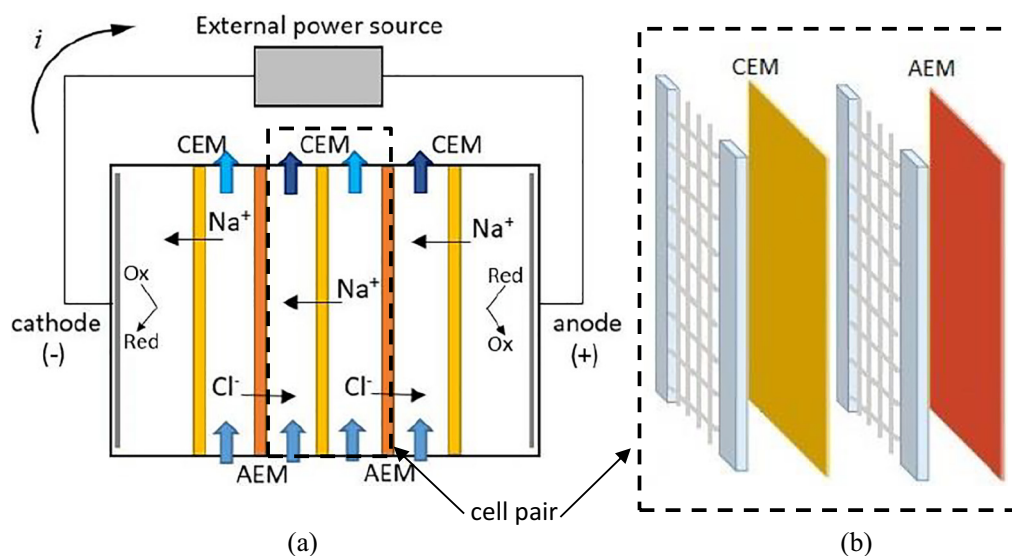 E-mail address: luigi.gurreri@unipa.it (L. Gurreri).

Fig. 1. Schematic representation of a) ED stack and b) cell pair in a parallel flow configuration.

1. Introduction

Electrodialysis (ED) is a membrane process known since 1890, but applied for water desalination only since the 1950s [1–3], when the first suitable ion-exchange membranes were commercially available [4, 5]. An ED stack, illustrated in Fig. 1a, consists of the repetition of a periodic unit, called cell pair (Fig. 1b), which includes a cation exchange membrane (CEM), a diluate compartment, an anion exchange membrane (AEM) and a concentrate compartment. The spacing between membranes is maintained by inserting polymeric spacers. A net with overlapped or woven filaments is the most frequently used spacer in membrane processes [6].

Electrodialysis has become of increasing relevance in the last decade, e.g. in the production of high-quality industrial process water and the treatment of industrial effluents [7, 8]. A combination of ED and brackish water reverse osmosis (BWRO) was proposed by Galama et al. [9] as an alternative to seawater reverse osmosis (SWRO). The application of multistage ED to seawater desalination is also currently studied [10].

The performance of the ED process is improving due to the research efforts towards producing high-performing ion-exchange membranes [11]. However, real membrane properties still have an important role in limiting the performances, especially non-ideal permselectivity and water permeability. The minimum energy consumption, expected for seawater desalination, may increases by a factor of 3 if co-ions flux is considered and by about 10% when also the water flux is considered [12, 13]. Aside from the membrane properties, the performance of an ED stack can be affected by other parameters or phenomena, among which the most relevant is concentration polarization.

According to the IUPAC Recommendations, concentration polarization is defined as "a concentration profile that has a higher (or lower) level of solute nearest to the upstream membrane surface compared with the more-or-less well-mixed bulk fluid far from the membrane surface" [14]. An example of concentration profiles in the concentrate and diluate compartments is reported in Fig. 2a.

These profiles arise because the kinetics of transport in solutions and in membranes are different, which leads to enrichment and depletion layers next to the membranes. This phenomenon can also be explained by considering the transport numbers, which are higher in membranes than in solutions ($T > t$): moving from the solution to the membrane, the migrative flux of counter-ions increases and a concentration gradient arises in the liquid phase [15].

Observing the diluate channel, the concentration at the membrane surface decreases and, according to the classical theory of concentration polarization in an electroneutral solution [18], when the electrolyte concentration at the interface approaches zero, the diffusion-limited current density is reached [19, 20]. This condition corresponds to a plateau in the current-voltage curve (Fig. 2b).

According to this theory, the first predictions of the limiting current density was proposed by Peers [21] in 1956. In the Peers equation (see Table 1) δ is the diffusion boundary layer thickness. This is often defined as the distance from the membrane to the cross point of the tangents drown to the concentration profile at the interface and in the bulk solution [22]. In the literature, the Lévêque equation [23, 24] is more commonly adopted: it is derived from the Peers equation and the Graetz-Lévêque theory of developing laminar flow through spacerless channels, and it is valid for membranes characterized by a short length, i.e., when $(LD)/(H^2u) < 10^{-2}$, and homogenous surface [25]. Among the most recent models proposed in the literature to estimate LCD, Geraldes and Afonso [26] considered the electrodialysis of multi-ionic solutions: using a linearized form of the Nernst–Planck equation together with the electroneutrality condition at the solution/membrane interface, they deduced an explicit expression of LCD, which requires the effective diffusivity of the multi-ionic solution. Nakayama et al. [27] started from the Nernst-Planck equation, which they reduced to a convection-diffusion transport equation with an effective diffusion coefficient by eliminating the electrophoresis term. This equation was then applied in the boundary layer, by using the principle of similarity of the classical boundary layer theory [28], in order to obtain asymptotic results for concentrations, limiting current density and stack voltage, for long and short ED channels.

All the above models can predict the plateau in the current-voltage curve (Fig. 2b), which can be observed only in simple electrochemical cells in which a single solution-filled channel is limited by two electrodes. In these cases, the diffusion-limited current density is univocally determined by the plateau. When ion exchange membranes (IEMs) are present, as in the case of real ED stacks, there is no actual saturation of current: as illustrated in Fig. 2c, the current does not exhibit a marked plateau but rather a region of slow increase which merges without a sharp transition with a third region, the overlimiting region [29]. The appearance of this last region was initially attributed to the loss of permselectivity and the transport of H^+ and OH^-, produced by a water splitting reaction. These phenomena, however, were later identified as often non-dominant contributions to the overlimiting current: in fact, even for currents much larger than the diffusion-limited value, charge is mainly transported by salt ions and the contribution of water splitting is