Electrolysis in thin layer: A technique for electroanalytical and electrosynthetic applications

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Abstract

Thin-layer electrochemistry deals with electrochemical reactions in a confined solution comparable to the thickness of the diffusion layer. It gives immediate access to the electrode surface for performing rapid electrolysis reactions. The aim of this article is to highlight the seminal studies and some recent updates on thin-layer electrochemistry in three sub-sections: a) batch-type thin-layer electrodes (TLEs) and their principles, b) optically transparent TLEs for in situ spectral observation of the electrode reaction, and c) thin layer flow microreactors focusing on paired electrochemical reactions.

Keywords: Thin Layer Electrochemistry, Spectroelectrochemistry, Flow Microreactor.

Introduction

The heterogeneous nature of electrochemical reactions requires considering both electron transfer and mass transfer processes [1], and for the preparative electrolysis reactions, the latter becomes more prominent [2]. For most electrolysis experiments, the desired reaction happens in the diffusion layer, while the completion of the reaction requires all the substrate molecules present in the solution bulk to reach the diffusion layer [3,4]. The time scale of the electrolysis experiment is determined by the convective mass transfer, the design of electrochemical cells, and the ratio of the electrode surface area to the cell volume (A/V ratio) [5]. Mass transport limitations resulting from the cell design are considered the intrinsic constraints of bulk electrolysis and electrosynthesis, especially for batch-type cells [6]. One approach for omitting inbound convective mass transfer of electrolysis reactions is to confine the electrolysis solution to a thin layer, comparable to the thickness of the diffusion layer, at the electrode surface [7]. No convection occurs in this confined solution with submillimeter thickness, and diffusion is the sole mass transfer mechanism. Expanding the diffusion layer in this thin, confined solution requires a few seconds to minutes of electrode reaction, i.e., 10 sec for 0.01 cm expansion, assuming the diffusion coefficient equals $5.0 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ [4]. This approach that relies on a thin layer electrode (TLE) enhances the A/V ratio (drastically) and makes it possible to perform rapid electrolysis within a time scale similar to the electroanalytical experiments in a small solution volume [1].

Batch-type TLE

Early examples of exploiting this approach, reported by Anson, included two types of TLE called wire electrode and plate electrode. Wire electrode was made by confining the solution between a Pt wire (with 0.076 cm diameter) and glass tubing. The gap was introduced by the electrodeposition of copper on Pt wire and its electrochemical dissolution after inserting and sealing the wire in a soft glass tube by heating (Figure 1a). The thickness of the TLE was 1.5×10^{-3} cm, which was the same as the thickness of the dissolved copper layer. The basis of plate TLE was making a gap with uniform distance between a flat glass and a Pt disc using a thin insulating gasket, i.e., 0.01 cm polyethylene (Figure 1b) [8–10]. After filling the thin layer cavity (for wire electrode) or the thin layer gap (for plate TLE) with the desired solution, the electrodes were immersed in an electrolyte solution bearing the working and reference electrodes. The connection between the electrolyte solution and the entrapped TLE solution was made through the cavity opening for wire TLE, and the gasket's slit for plate TLE. Using wire TLE with an A/V ratio of >600 cm^{-1} and a solution thickness of 0.0015 cm, theoretically, it takes <1 second for the diffusion layer to expand in TLE. Recording cyclic voltammogram (CV) of Iron ion (Fe^{2+}) in the thin layer demonstrates a bell-shaped plot that is symmetrical about the peak potential and returns to the baseline at the end of the anodic cycle [11], indicating the complete consumption of entrapped Fe^{2+} within the time scale of the voltammetric experiment (forward scan). Similar CV features in the backward scan indicate the consumption of electrochemically generated Fe^{3+} without diffusive leak through the TLE opening (Figure 1c).

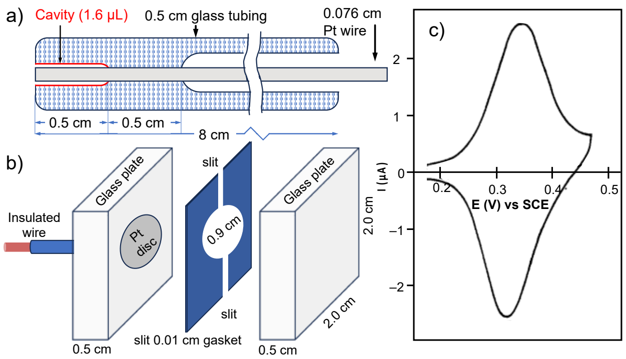

Figure 1. *Schematic drawings of a) wire and b) plate TLE. c) cyclic voltammogram of* Fe^{2+} *recorded using wire TLE, adopted from Ref* [9,11]. *The axes directions were changed based on IUPAC convention.*

Various other setups have been explored, and the theory of thin-layer cells has been developed within a few years. Thin-layer cells were used in a number of electrochemical studies, including n-value (number of electrons) determinations, investigations of electrodeposition and adsorption, and studies of coupled chemical-electrochemical reactions [7,10–18]. Considering the size and thickness of the TLE, the reference and counter electrodes are placed outside the thin-layer chamber. This causes nonuniform potential and current distributions resulting from high uncompensated ohmic drops in a thin solution layer [17]. Additionally, with this high A/V ratio and the small opening of TLE to the outside solution, the charge transfer from and to the TLE may become a limiting factor for the electrode process and current. Therefore, careful control of the experimental parameters and conditions must be considered for accurate data collection and interpretation. For example, voltammetric experiments must be performed at low scan rates, typically < 10 mVs^{-1} [11]. For fast voltammetric experiments that high current is expected, charge transfer from/to the TLE limits the current, leading to a plateau current for voltammetric responses [17]. Moreover, the separation of reaction products and further characterization are either challenging or impossible for most batch-type setups. Therefore, batch-type thin-layer electrochemical cells were used only for electroanalytical applications and not for synthetic applications. Finally, the development of TLE overlapped with the rise of other electroanalytical techniques, with more universal and less technical cell setups [19]. These electroanalytical techniques, especially various voltammetric techniques, outcompeted the TLE-based electroanalytical techniques. The literature on using TLEs as electroanalytical tools was rather scarce in the past half-century. Aside from these considerations, small-scale reactions and minute-scale electrolysis time are the attractive aspects of TLE that remained unexplored and, with the advancement in cell and electrode fabrication techniques, need to be reconsidered.

An example of recent TLE is the work of Marzouk and coworkers on developing a chip-type TLE that accommodates commercially available screen-printed electrodes (SPE) for batch or flow electrochemical reactions [20]. Kim and coworkers presented a thin-layer electroanalysis microchip (TEAM) to exploit the advantages of classic TLE for mechanistic studies of electrochemical reactions (Figure 2a) [21]. The microliter-scale analytical volume of TEAM and rapid electrolysis reactions made detecting the reaction intermediates and accurate n-value determination of some organic electrochemical reactions feasible [22]. One of the common findings of these two reports was that thin-layer-based chip cells produced better-resolved voltammetric peaks than semi-infinite diffusion because of the complete current decay around the peak under thin-layer conditions. This enhanced resolution is appealing in mixture analysis or electrochemical analysis of the reactions with more than one electroactive component [20]. A pipette-type TLE was developed in this laboratory for facile loading and offloading the sample to the TLE [23]. The pipette-type structure of TLE, with 10 µL to 100 µL volume, allows easy separation of the products of electrolysis reactions (Figure 2b). Separating out the TLE solution from the cell solution (where reference and counter electrodes are placed) means the effect of counter electrode reaction can be neglected without the concern of divided or undivided setups. It also highlights the advantages of using multiple TLEs in one cell instead of multiple cells for parallel reactions, which is promising for high-throughput experimentation (Figure 2c). Finally, the design of the TLE allows the accommodation of a microelectrode within a micrometer distance from the electrode surface of the TLE. It makes it possible to probe the concentration profile of electroactive species in real-time [23].

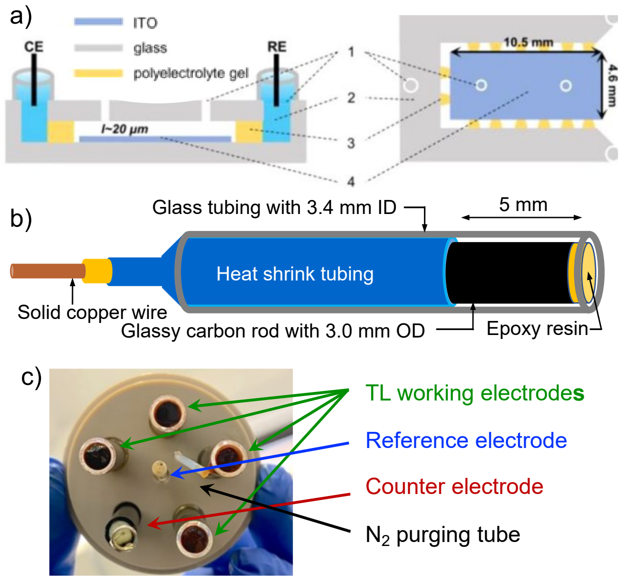

Figure 2. *Schematic drawing of a) TLE microchip adopted from Ref [22], b) a pipette-type TLE, and c) bottom view of the electrode assembly with four TLEs for parallel electrolysis reactions adopted from Ref* [23].

Optically Transparent TLE

One approach for fabricating the TLE is to confine electrolysis solution between two pieces of glass, similar to the plate TLE by Anson, in which a) the surface of the glass is conductive and acts as the working electrode [13], or b) inserting a mini-grid working electrode in TLE [16]. This provides an optically transparent TLE (OTTLE) that enables rapid electrolysis reactions and concurrent spectral data acquisition. The coupling of spectrochemical and electrochemical techniques, known as spectroelectrochemistry [24,25], was employed to investigate various inorganic [26–28], organic [29,30], and biological redox reactions [31,32], over the past 6 decades. The basis of all these spectroelectrochemical techniques is rapid electrolysis in TLE for real-time monitoring of the species with a half-life exceeding several seconds, avoiding interference of unreacted substrates in solution bulk, and verifying the nature of the electrolysis products by spectroscopy without further separation. A variety of spectroscopic techniques have been employed for spectroelectrochemical studies [33–35]. However, UV-visible spectroscopy is the most common technique considering the electronic and structural changes in molecules during electrochemical processes and the solution-based media of the reactions [36]. Commercially available OTTLEs are available based on the initial concept of using mini-grid electrodes and transparent conductive glasses. One recent example of using OTTLE for UV-visible spectroelectrochemical studies is the work by Kishioka, which studied the oxidation of violuric acid. Figure 3c shows the spectral change during the oxidation of violuric acid, and Figure 3d shows the absorbance-potential profiles for violurate and its electrochemically generated neutral radicals at their maximum absorbance, at 242 and 311 nm, acquired simultaneously during a slow scan (0.5 mVs^{-1}) cyclic voltammetry experiments [37].

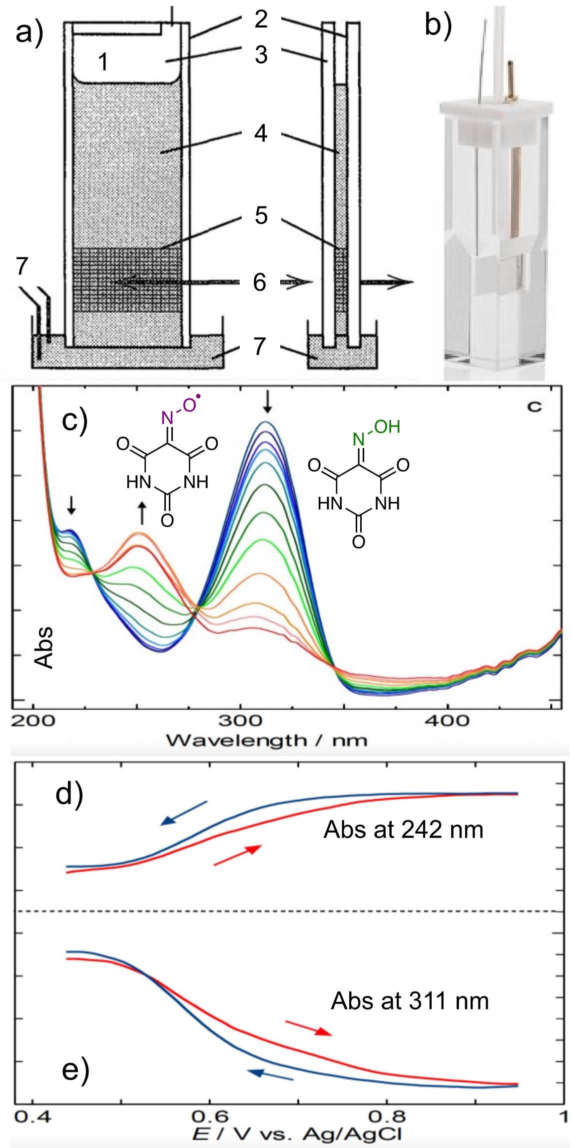

Figure 3. *Schematic drawing of an early example of OTTLE; b) commercially available OTTLE for UV-Vis spectroelectrochemical studies; c) spectral change of violurate by changing the potential and d) and e) the absorbance-potential profiles at maximum absorbances of each redox species, acquired during a cyclic voltammogram at 0.5* mVs^{-1}*, adopted from Ref* [37].

Thin Layer Flow Microreactor

Electrochemical flow reactors with narrow channels and a relatively large A/V ratio, compared to batch-type reactors, have more connection to thin-layer electrochemistry. Extremely high A/V ratios can be achieved using channels with a few micrometers to submillimeter thickness, which is the prime advantage of a flow microreactor [38]. Various electrochemical flow microreactors with different interelectrode gaps with divided and undivided configurations have been developed, and their theory and applications have been developed and reviewed in depth [38–42]. Herein, we highlight the advantages of working in flow microreactors with thin interelectrode gaps in which diffusion layers of the electrodes (anode and cathode or working and counter electrodes) could overlap. This can be utilized for reactions between highly reactive intermediates generated by both anodic and cathodic reactions. The concept is known as paired electrosynthesis, and for reactive intermediates, the required time for mass transfer from the originating electrode to the counter electrode hampers using it. Buchwald and co-workers engineered a microfluidic TLE for a variety of redox-neutral paired electrochemical reactions involving reactive radicals [43]. One example was a cross-coupling reaction between the radicals resulting from oxidative decarboxylation of carboxylic acids and the reduction of electron-deficient aryl nitriles (Figure 4a). They demonstrated that the product yield decreased with an increase in the interelectrode distance from 25 μm to 500 μm, and the highest cross-coupling product yield was achieved at a 25 μm interelectrode gap, and the yield was higher than traditional batch-type cell. Atobe and coworkers also demonstrated the use of a TLE for a variety of applications, including spectroelectrochemical reactions [44]

Another instance of paired electrochemical reactions using a flow microreactor (TLE) was demonstrated by Atobe and co-workers. They achieved a reasonable yield (74%) in transforming benzylamine into dibenzylamine using an electrochemical flow microreactor characterized by a narrow interelectrode gap of 0.08 mm [45]. The process involved oxidative condensation of benzylamine to N-benzylidenebenzylamine at the anode surface, followed by its diffusion (to cathode) and reduction to dibenzylamine (Figure 4b). A comparative analysis of the product yields and selectivity using a conventional batch reactor and different microreactors was conducted. It revealed that >95% conversion of benzylamine was achieved using 0.08 mm flow TLE and batch cells, but N-benzylidenebenzylamine to dibenzylamine ratios were 58:42 and 97:3, respectively. This comparison underscores the impact of a short interelectrode gap (TLE) in facilitating paired electrosynthesis [45,46].

Atobe and co-workers reported the use of a two-inlet microflow electrochemical reactor, featuring a 0.02 mm interelectrode gap, for the generation of N-acyliminium ions and their subsequent reactions with an oxidizable nucleophile, allyltrimethylsilane (Figure 4c) [47]. In this operational setup, the cation precursor solution and nucleophile solution are introduced in parallel, ensuring that minimal oxidation of the nucleophile occurs at the anode. Instead, the cation precursor undergoes oxidation exclusively at the anode surface, and the resulting cations diffuse through the solution to react with the nucleophile, leading to a substitution reaction with a 91% yield.[47,48]

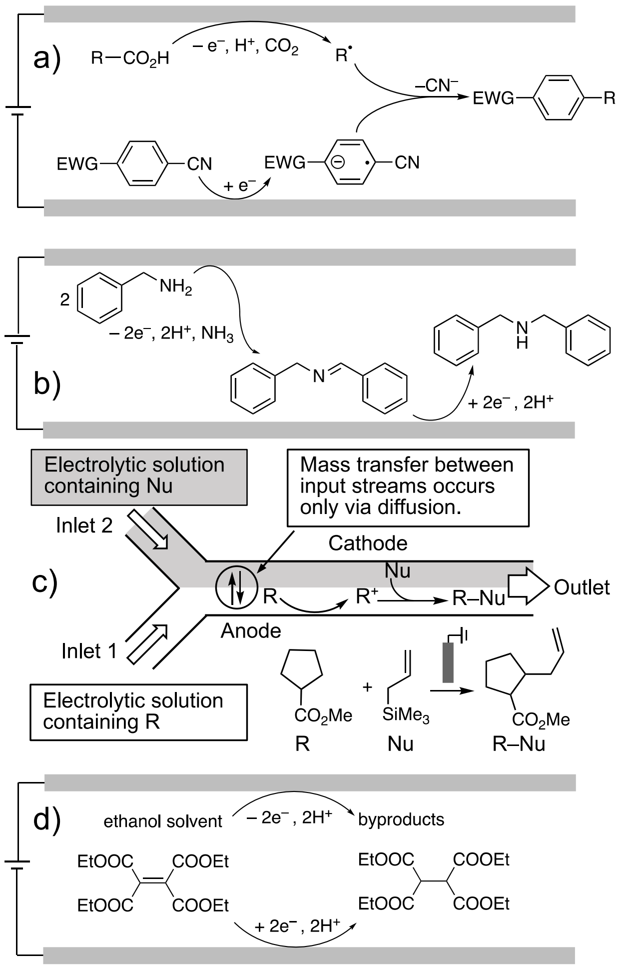

Figure 4. *Examples of electrochemical reactions used in a flow-thin layer: a) redox-neutral paired electrochemical reactions adopted from Ref* [43]*; b) paired electrosynthesis with tandem anodic and cathodic reactions adopted from Ref* [45]*; c) paired electrolysis with two inlets adopted from Ref* [43]*; and d) electrolysis with no supporting electrolyte adopted from Ref* [49]*.*

The proximity of electrodes reduces the ohmic voltage drop in the electrolyte, facilitating electrolysis using low concentrations of supporting electrolyte or under electrolyte-free conditions [49,50]. This concept was demonstrated by Marken and coworkers using an undivided parallel plate-to-plate flow microreactor with a 0.1 mm interelectrode gap [49]. In this configuration, diffusion layers from each working electrode and the counter electrode overlap, leading to the formation of a conductive layer (by electrochemically generated ions) in the absence of additional supporting electrolytes. In proof-of-principle experiments, they examined the reduction of tetraethyl ethylenetetracarboxylate to tetraethyl ethanetetracarboxylate in ethanol solvent without intentionally adding electrolyte (Figure 4d). Proton-coupled electrooxidation of ethanol solvent provides the protons to make the thin layer environment conductive and furnishes the proton-coupled reduction at the cathode. This concept was later reported and proved by other studies.

Conclusion

In conclusion, the concepts of batch TLE, spectroelectrochemistry, and flow microreactor were presented, considering thin-layer electrochemistry as their common characteristics. The concept of batch TLE is still unexplored, even with a half-century background. This perspective aimed to draw attention to the advantages of batch TLE, including immediate access to the electrode surface, a simple mass-transfer regime, and rapid electrolysis time, highlighting its similarities to the two well-stabilized latter thin layer-based techniques.

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