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2021

Goh, G. L., Tay, M. F., Lee, J. M., Ho, J. S., Sim, L. N., Yeong, W. Y. & Chong, T. H. (2021).
Potential of printed electrodes for electrochemical impedance spectroscopy (EIS) : toward
membrane fouling detection. *Advanced Electronic Materials*, 7(10), 2100043-.
<https://dx.doi.org/10.1002/aelm.202100043>

<https://hdl.handle.net/10356/152414>

<https://doi.org/10.1002/aelm.202100043>

This is the peer reviewed version of the following article: Goh, G. L., Tay, M. F., Lee, J. M., Ho, J. S., Sim, L. N., Yeong, W. Y. & Chong, T. H. (2021). Potential of printed electrodes for electrochemical impedance spectroscopy (EIS) : toward membrane fouling detection. *Advanced Electronic Materials*, 7(10), 2100043-, which has been published in final form at <https://doi.org/10.1002/aelm.202100043>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

Potential of Printed electrodes for Electrochemical Impedance Spectroscopy (EIS): Towards Membrane Fouling Detection

Guo Liang Goh¹, Ming Feng Tay², Jia Min Lee¹, Jia Shin Ho², Lee Nuang Sim², Wai Yee Yeong^{1*}, and Tzyy Haur Chong^{2,3}

¹Singapore Centre for 3D Printing (SC3DP), School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798

²Singapore Membrane Technology Centre, Nanyang Environment & Water Research Institute (NEWRI), Nanyang Technological University, Singapore 637141

³ School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798

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Abstract

Electrochemical impedance spectroscopy (EIS), one of the techniques for electrochemical analysis, has been used for a wide range of applications especially chemical- and bio-sensing. Besides, EIS is one of the few that has been proven useful for membrane fouling detection. Electrodes are some of the most essential components for analytes detection applications with EIS. With the advances in printing technology, the fabrication of advanced printed electrode systems with miniature designs and improved sensitivity for electrochemical sensing is made possible. This review addresses recent advances in printed electrodes for electrochemical impedance spectroscopy with the emphasis placed on discussing the use of printed electrodes for membrane fouling detection. Common electrode designs and materials for electrochemical impedance spectroscopy are discussed, along with practical examples of these printed electrodes. The commonly used printing techniques for the fabrication of printed electrodes are also deliberated. The successful realization of printed electrodes for EIS requires careful design of electrodes, proper selection of electrode materials, as well as optimization of the printing process. It is expected that printed electrodes will be widely accepted for EIS sensing applications and will facilitate the creation of low-cost high-performance sensing devices.

Keywords – Electrochemical impedance spectroscopy, printed electrodes, nanomaterials, sensing and monitoring, membrane fouling monitoring

1. Introduction

Detection of analytes has become important in the current age as it is extensively used in various fields such as point of care medical diagnosis ^[1-3], detection of pollutants for environmental assessment ^[4], food quality analysis ^[5, 6], and system health monitoring ^[7]. Often, the analytes can be detected and analyzed by electroanalytical methods such as capacitance method, coulometry, amperometry, potentiometry, voltammetry, and impedance spectroscopy ^[8]. With the advanced development of the sensor technology over the past decades, modern electroanalytical methods play an increasingly

important role in the field of biological and environmental analysis^[9-12]. A variety of sensors made of glassy carbon, nanocomposite, and metal-organic framework-based materials (MOFs) have been rapidly developed to allow for a deeper understanding of the multi-electron transfer systems and high accuracy and precision measurement.^[13-18] These electroanalytical techniques offer superior benefits such as low detection limit, high level of simplicity, low equipment cost, and high fidelity^[19].

Electrodes are important component to form a complete electrochemical cell for analytes analysis^[8]. These electrodes are commonly made up of conductors such as gold, platinum, and carbon^[20]. Depending on the type of analytes, the choice of the working electrode depends mainly on the redox behavior of the target analytes, and the background current over the applied potential region^[20]. Many studies have shown that the selectivity and sensitivity of the analytical devices do not only depend on the innate material property of the electrodes, but they can also be enhanced by surface modifications either by physical, chemical, or biological means^[21].

Over the years, the design of the electrode has transformed from a simple cylindrical electrode design to a more complex planar microelectrode design such as the interdigitated electrodes and the microelectrodes arrays^[22]. For decades, such complex planar microelectrode design is achieved by using conventional lithography, silicon chip, and cleanroom technologies which are often costly and time-consuming^[23, 24]. Besides, the microelectrodes fabricated using these technologies are often rigid and brittle as they are fabricated on silicon wafers as the substrate material. With the focus of the industry shifting towards the use of low-cost and high-throughput technology, the fabrication of electronic components including the electrodes using additive manufacturing (or 3D printing) approaches has been widely adopted^[25]. Printed electrode is getting more attention because it provides numerous benefits such as (1) the ability to process a wide range of substrate materials including flexible materials and (2) shorter time for prototyping and fabrication process compared to the conventional method^[26].

Among the electrochemical methods, EIS has been identified as a powerful tool for the analysis of systems with complex electrical resistance and it is sensitive to the changes of surface properties as well as bulk properties^[27]. One of the outstanding applications of EIS is the detection of fouling phenomena in reverse osmosis (RO) membrane used for wastewater/water reuse applications^[28-31]. Apart from that, EIS has also been employed for the characterization of different types of membranes, including biological^[32-34] as well as synthetic membranes^[35-42]. EIS is capable of detecting membrane fouling based on the distinctive trend recognized in the diffusion polarization (DP) layer throughout the filtration process. In addition, EIS has been utilised in various applications which includes corrosion

detection^[43], material degradation^[44], chemical sensing^[45], biosensing^[46], and characterization of energy harvesting^[47] and storage devices^[48].

To date, various electrode designs and systems have been developed for EIS applications, however, there has been no review to summarize the available designs, materials, and fabrication techniques for such printed electrodes to the best of the authors' knowledge. This review, therefore, focuses on reviewing (i) different printed electrode designs; (ii) the materials selection for printed electrodes, and (iii) different fabrication techniques for printed electrodes. Emphasis has been placed on discussing the design and materials of printed electrodes for EIS sensing applications. Lastly, the state-of-the-art printing techniques for electrode printing and various applications of printed electrodes for EIS method are discussed.

2. Electrochemical Impedance Spectrometry

2.1 Principle of EIS

Electrochemical impedance spectroscopy (EIS) is a perturbative characterization of the dynamics of an electrochemical system. The fundamental approach of the EIS is to measure the current, voltage, or any other signals of interest in response to an applied sinusoidal excitation signal to a system under investigation. EIS measurements can be done in the potentiostatic or galvanostatic mode depending on the application of interest. However, the investigation by either potentiostatic or galvanostatic EIS is comparable and likely to produce similar results in most cases. There are only a handful of application-specific conditions where one technique is more suitable than the other. In galvanostatic mode, the EIS measurements are performed by injecting a sinusoidal alternating current (a.c.) of known frequency, ω and amplitude i_o into the system and measuring the voltage, v_o across the measuring sample. The input sinusoidal current is represented as^[49]:

$$i = i_o \sin(\omega t) \quad (1)$$

The response is similarly sinusoidal, as follows:

$$v = v_o \sin(\omega t - \theta) \quad (2)$$

θ is the phase difference between the two sinusoidal signals and is measured during the impedance measurement. The response of the system to a change in potential is not instantaneous and this causes the responding current to lag. The cause behind this behavior is that every electrochemical cell has a capacitive contribution: the charging and discharging of a capacitor when the potential changes is not an instantaneous process.

Impedance is a complex quantity and it is described by the combination of resistance (R) and reactance (X) as follows:

$$Z = R + jX \quad \text{where } j = \sqrt{-1} \quad (3)$$

Resistance is present in components that are resistive, most notably, the resistors. On the other hand, reactance can exist in two forms which include capacitive and inductive elements. The impedance is typically represented by a phasor in which the magnitude and the phase are defined as follows:

$$|Z| = \frac{v_o}{i_o} \quad \text{and} \quad \angle Z = \theta \quad (4)$$

By performing Laplace transforms of the sinusoidal functions (Eq. 1 and Eq. 2), the impedance can be presented in the following form ^[49]:

$$Z = TF(j\omega) = \frac{v_o}{i_o} \cos \theta + j \frac{v_o}{i_o} \sin \theta \quad (5)$$

The impedance for a homogeneous material can be represented using a Maxwell-Wagner element where a conductance element G is connected in parallel with a capacitance element C , expressed as follows:

$$Z(\omega) = \frac{1}{G + j\omega C} \quad (6)$$

As such, by combining Eq. 5 and Eq 6, the conductance (G) and capacitance (C) of the element are defined as:

$$G = \frac{1}{|Z|} \cos \theta \quad (7)$$

$$C = -\frac{1}{\omega |Z|} \sin \theta \quad (8)$$

where the parameter G describes the ability of the sample of interest to conduct while the parameter C describes the capability of the sample to store electric charge.

One advantage of EIS technique is that the mean potential across the electrodes is zero because of the small alternating current (AC) signal that is used for perturbing the system ^[50]. With the spectroscopic measurements, electrical and electrochemical information can be used to indicate the nature of analytes and their interaction with the electrodes ^[50].

2.2 Applications of EIS for sensing

Among the different types of mechanical and optical transducers (e.g. cantilever biosensors, surface plasmon resonance-based biosensors), electrochemical sensors have been widely adopted for biological application. One major advantage is that electrochemical sensing allows in situ detection of

target with minimal to no sample preparation. Electrical/electrochemical impedance measurement has been widely used in biological applications ^[51, 52], where analytes can vary in terms of scale – from detecting specific DNA sequences in disease diagnostic, to impedance measurement of cells ^[53] and detection of endogenous chemical products such as neurotransmitter ^[54]. For instance, a label-free paper-based sensor was designed with pyrrolidinyl peptide nucleic acid as probes, for the detection of *Mycobacterium Tuberculosis* (MTB) ^[55]. The probes were immobilized onto cellulose paper, where MTB was measured by the fractional changes in the charge transfer using EIS. EIS sensing offers quantitative detection of DNA with improved sensitivity and selectivity while providing a lower detection limit as compared to colorimetric detection. Hadi and team formulated a carbon paste electrode for detection of topotecan, a type of chemotherapy drug, in urine and serum samples. Double-stranded DNA was immobilised on carbon paste electrode and the modified electrode demonstrated exceptional features such as high sensitivity and selectivity, reproducibility and stability ^[11].

EIS with its advantage as a non-destructive measurement is ideal for assessing the state of cells and tissues during cell culture. Impedance data could be used to directly determine the growth rate of cells ^[56]. The value is directly related to the population dynamics, where increased cell population resulted in increased impedance. Omar Din et al engineered bacteria containing lysis gene where upon lysis, the conductive properties of the culture change drastically ^[57]. This setup can be used for metal toxin sensing, where exposure to heavy metals such as arsenic changes the admittance and turbidity of cell culture. Impedance spectroscopy has also been used to monitor the state of cells. For instance, changes in cell layer capacitance are used to assess the differentiation state of the human intestinal epithelium in real-time ^[58]. A larger surface area associated with villi formation is associated with decreased epithelial resistance and increased capacitance. Impedance cell sensors have been designed to monitor stem cell differentiation ^[59, 60]. EIS offers a method to capture changes in cell morphology, and in combination with monitoring mass changes, provides quantitative information regarding the process of stem cell self-renewal and differentiation ^[60].

EIS has also seen its application in surgical settings where sensors are integrated onto needles to assist in the biopsy collection ^[61-63]. To resolve the inaccuracy of the image-guided biopsy process, biopsy needles incorporated with multi-modal sensor arrays were designed to sense variation in pH, glucose, and electrical impedance ^[62]. pH of cancerous tissue is generally lower than normal tissue, whereas the uptake rate of glucose in cancer tissue is quicker than normal tissue. Cancerous tissue has higher impedance as it is higher in cellular density as compared to normal tissue ^[61]. Sensor integrated biopsy

needle exploited the electrical characteristic of cancer tissues to surmount the weakness of the traditional image-guided biopsy procedure.

Apart from the biological applications, EIS has also been applied widely in membrane fouling detection in the water treatment process and this will be described in detail in the following sections.

3. Membrane Fouling Detection

3.1 Membrane Fouling

Membrane fouling is a process of the buildup of unwanted substances on the membrane surface which can lower the filtering efficiency of the membrane ^[64]. Fouling is a complex phenomenon that involves various mechanisms under different filtration conditions. The fouling mechanisms of low-pressure filtration operation, such as microfiltration (MF) and ultrafiltration (UF) can be different from those of high-pressure membranes, i.e., nanofiltration (NF) and RO ^[65]. For example, the main fouling mechanism for NF and RO is cake filtration whereas, both pores blocking and cake filtration could be involved in MF and UF filtration. Membrane fouling can be generally categorized into several types (i.e., colloidal fouling, organic fouling, scaling, and biofouling) based on the different types of foulants involved. Membrane fouling is an unavoidable phenomenon in membrane filtration process. The undesired consequences as a result of fouling include flux decline, deteriorated membrane rejection, poor permeate quality, shorter membrane lifespan, and higher energy cost ^[66]. Despite the tremendous effort and research on preventing and controlling fouling, it is still the major obstacle that limits and slowdowns the deployment of membrane technology in various industries to date.

As such, researchers have been exploring different ways to better monitor membrane fouling ^[67, 68]. The conventional approaches for detecting fouling (i.e., monitoring the pressure drop across the modules, flux decline rate, and the water product quality) often indicate the late stage of fouling where mitigation strategies are often ineffective. This will result in higher hydraulic pressure required for the desalination process which translates to high operating energy and cost for the desalination plant. One approach to better control membrane fouling is to detect fouling at its early stage and identify the types of fouling. With this information, an appropriate cleaning protocols can be actuated in time to prevent excessive fouling.

Many studies have shown the effectiveness of EIS in detecting membrane fouling in the RO process ^[7, 39]. One of the unique features that EIS technology can offer is its ability to identify the fouling types. More importantly, it is capable of identifying early fouling based on the minor changes in electrical properties on the membrane surface well before the fouling reaches an irreversible stage. This is of

paramount importance to the formulation of effective fouling mitigation strategies to ensure the long-term sustainable operation of the desalination plant.

3.2 Principle of EIS in membrane characterization

In this section, the theoretical background of EIS with an emphasis on membrane characterization and fouling detection will be presented. EIS is able to provide information on the conductive and capacitive properties of a system. It is also known to be a valuable technique to characterize the different sub-structural layers within a membrane [36, 49].

Taking a membrane system as an example, the electrical impedance of a typical reverse osmosis membrane can be modeled to a first approximation by the circuit shown in Figure 1b. The total impedance of the equivalent circuit for this membrane system is a function of frequency represented by Eq. 9. For a heterogeneous system (i.e., membrane system) comprised of several electrically distinct layers, the total impedance for such system is given by [36, 49]

$$Z_N(\omega) = \sum_{n=1}^N \frac{1}{G_n + j\omega C_n} \quad (9)$$

where n indicates the n th layer. This is commonly known as the Maxwell-Wagner model, represented by several electrical circuits (a parallel combination of conductance and capacitance elements) connected in series.

Figure 1. (a) SEM image of a cross-section of a RO membrane (BW30) showing three distinct layers: polyamide (PA) skin layer, polysulfone (Psf) substrate, and polyester (PE) non-woven fabric layer. (b) An equivalent circuit of membrane and solution system. The skin, the substrate, and the non-woven layer of the membrane are represented by a circuit comprising of a conductance, G , and capacitance, C , element. [Reprinted with permission from ref [69]. Copyright 2016 Elsevier]

Thus, by measuring the dispersions of the overall conductance, $G(\omega)$, and capacitance $C(\omega)$ of the membrane and the solution, it is possible to show the presence of dielectric layers in the system. Furthermore, mathematical algorithms have been derived to deduce the contribution of each

individual layer from the measured impedance dispersion of both the magnitude and phase ^[49]. With this information, it is possible to further reveal the layer's geometrical properties, such as the dielectric thickness (d_n) as given by ^[36].

$$d_n = \frac{\varepsilon_n \varepsilon_0}{C_n} \quad (10)$$

where ε_n is the dielectric constant of the n th layer and $\varepsilon_0 (= 8.85 \times 10^{-12} \text{ Fm}^{-2})$ is the permittivity of free space.

Besides the typical bode plot (where the measured impedance is plotted over a range of frequencies), Nyquist plot is another useful representation of the EIS data, which gives a direct view of the presence of numerous elements in the process. The total impedance of the system (Equation 6) can also be represented in the following expression:

$$Z(\omega) = \frac{G}{G^2 + C^2 \omega^2} - j \frac{C\omega}{G^2 + C^2 \omega^2} \quad (11)$$

Since Z is a complex variable, $Z = Z_{\text{Re}} - jZ_{\text{Im}}$ where Z_{Re} represents the real part of Z and Z_{Im} refers to the imaginary component of Z . Hence,

$$Z_{\text{Re}} = \frac{G}{G^2 + C^2 \omega^2} \text{ and } Z_{\text{Im}} = \frac{C\omega}{G^2 + C^2 \omega^2} \quad (12)$$

Figure 2a illustrates an example of the Nyquist plot of a clean RO system and its theoretical fit using a Maxwell-Wagner model. When fitted with the Maxwell-Wagner model, it reveals more than four elements in the system. It is important to note that the equivalent circuit in Figure 1b is the first approximation of the RO system. In most cases, the model requires more theoretical electrical circuits to fit the measured impedance spectra. One of the reasons is that, in some of the cases, there was no sharp transition between the layers, (i.e. the adjacent layers have similar dielectric properties) ^[30].

Through the theoretical fitting on the EIS spectra, the characteristic frequencies of each element can be identified. Typically, at low frequencies (<10 Hz), there exists an element representing the diffusion polarization (DP) of ions at the membrane-solution interface. This phenomenon arises from a phenomenological event caused by the alternative accumulation and depletion of ions at the membrane-solution interface during the AC measurement. In RO filtration process, the DP layer was identified as the dominant layer where fouling occurs ^[28, 29, 31]. At mid frequencies, the dispersion in impedance can be attributed to elements representing membrane substrate and membrane skin layer. At higher frequencies (>10 kHz), there is an element representing the electrolyte connected in series with the membrane ^[28, 41, 69].

Figure 2: (a) Nyquist representation of a clean RO system. The full curves are theoretical fits using a Maxwell-Wagner model. (See the circuit diagram in the inset); (b) Element and deduced layer identity. [Reprinted with permission from ref ^[69]. Copyright 2016 Elsevier]

Coster and the co-workers have demonstrated the characterization of ultrafiltration (UF) membranes using EIS to characterize the conductance and capacitance of the skin and sublayers of the membrane ^[36]. Sim et al. later applied EIS to characterize the electrical properties of a RO membrane system ^[69]. The thickness of the support and polyamide layer determined using EIS was consistent with those measured using the microscopic methods. Apart from the characterization of polymeric membranes, the electrical properties of the supported ionic liquid membrane (SILM) were evaluated using EIS as well ^[37]. This study revealed the possibility of using SILM as proton conducting membranes and potential applications in electrochemical sectors.

3.3 Application of EIS in membrane fouling detection

Membrane fouling is the main limiting factor in RO technology. EIS has been successfully demonstrated in several studies as a real-time non-invasive fouling detection technique in the RO process ^[7, 28-31, 41, 69-71]. EIS is capable of distinguishing the impedance contributed by individual sub-layer (i.e., the membrane skin layer, membrane support layer, diffusion polarization layer, and bulk solution) based on their corresponding frequency ranges ^[49]. The great sensitivity of EIS to the variations in the interfacial layer in the RO filtration system could reveal meaningful information pertaining to the degree of fouling, change of concentration polarization, and foulant types in the RO

system. With this information at hand, the fouling control strategy can be formulated and implemented in time to ensure a sustainable RO operation.

The EIS system used for RO fouling detection typically consists of two current-injecting electrodes and two parallel voltage electrodes in a 4-terminal electrode arrangement. During the EIS measurement, a small alternating current (AC) of known frequency and amplitude is injected into the filtration system through the current-injecting electrodes and the voltage and phase difference across the membrane are detected by the voltage electrodes. These signals can then be used to determine the impedance, phase angle, capacitance, and conductance at different frequencies which correspond to the electrical properties of the internal and external layers of the membrane. EIS was first used to detect fouling of RO membrane by Kavanagh and the co-workers to monitor early-stage scaling of calcium carbonate in an osmotic pressure-driven cell ^[70]. They found drastic changes in conductance and capacitance at the onset of scaling. The electrode arrangement in the EIS system was redesigned for the high-pressure RO system and subsequently used for monitoring the colloidal fouling, organic fouling, and scaling ^[7, 30, 41, 71]. The EIS data is typically presented in a Nyquist plot with the negative imaginary impedance plotted against the real impedance fitted with the Maxwell–Wagner model. The shift in the plots could be identified as signals to the onset of fouling in the system which could not be identified previously by monitoring the TMP or flux decline.

In the RO application, the electrical properties of the membrane-solution interfacial layer (known as the diffusion polarization layer) are of greater interest as they correspond well to the variation of solutes in the interfacial layer (i.e., build-up of solutes/foulants near the membrane surface). This electrically distinct layer is identified at low frequencies (<10 Hz) ^[41]. The conductance and capacitance at low frequency were important indicators for the development of cake enhance concentration polarization (CECP) and the progress of fouling in the RO system ^[69]. The fouling type could be identified based on the changes in conductance, G_{DP} at the diffusion polarization layer. For example, an accumulation of organic solutes near the membrane surface corresponds to a decrease in G_{DP} while an increase in G_{DP} signifies an increase in inorganic solutes at this layer. Ho and the co-workers first attempted to use EIS to identify biofouling by observing closely G_{DP} . They discovered a consistent pattern in the G_{DP} plot that correlates well to the two stages in biofouling, i.e., initial bacteria attachment and biofilm development, resulted from the build-up of extracellular polymeric substances (EPS) ^[31]. The theory was further tested in a field trial study where the EIS was integrated into a canary cell to monitor fouling in a RO train ^[29]. This study showcased that EIS was capable of identifying the fouling types and development of fouling well before pressure drop and flux decline could be observed.

It is worth noting that membrane fouling is not unique to the RO process. In electrodialysis and membrane distillation (MD) processes, the process efficiency is significantly impacted by fouling. Several studies have demonstrated that EIS could be used to characterize fouling of anion exchange membrane and cation exchange membrane in electrodialysis (ED) process using the same underlying principles ^[72-75]. Park and the co-workers have developed a subtracting technique that could determine the changes in the capacitance and conductance arising from bovine serum albumin (BSA) fouling. It was found that the conductance and capacitance of the fouled ion-exchange membrane decreased with the accumulation of the BSA foulants on the membrane surface ^[72]. By monitoring the hindrance of transmembrane ion transport in the electrodialysis system, EIS could identify fouling due to the accumulation of anionic surfactants (i.e., sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS)) ^[75]. In addition, EIS was also successfully demonstrated for early wetting detection in the MD process ^[76, 77]. A recent study by Tian et al. has used EIS to monitor the change in the membrane distinct layers during the ultrafiltration of oil emulsions and the interactions of different types of surfactant with membranes were revealed ^[78].

3.3 Challenges of EIS in field application

Early fouling detection is critical for optimizing the fouling control strategies, for example, the protocol of cleaning-in-place (CIP) implemented in the RO desalination plant. As the state-of-the-art fouling detection technique, there is a huge potential for the EIS sensors to be deployed and integrated into the full-size desalination plants. However, the current EIS system is based on a side-stream canary cell, EIS-canary requires proper process control to mimic the hydrodynamic conditions in the actual spiral wound module (SWM). The high investment cost for equipment and process control system for EIS-canary cell makes the technology less attractive. To reduce the cost for wide deployment of the technology, a newly designed SWM with EIS sensors, known as EIS-module, is proposed where the electrodes and electronics are directly embedded in the SWM. The EIS-module can simply replace one of the standard elements in the pressure vessel in a RO train, as such no modification to the existing infrastructure is required and the filtration process is not interrupted while real-time information for the state of fouling can be obtained directly.

The rapid development in screen-printing technology has allowed the large-scale fabrication of low-cost and highly reproducible electrodes and sensors for on-site monitoring in the environmental fields. Printed electrodes have been used for numerous types of environmental analysis including the detection of heavy metal ions ^[79-81], pesticides and herbicides ^[82-84], phenolic compounds ^[85], bacteria and viruses ^[86], pharmaceutical medicine ^[87], etc. With the successful applications in the

environmental fields, printed electrodes have the potential here for early fouling detection for the desalination plant.

Nevertheless, creating a thin-film electrode that is cost-effective, flexible (bendable), and robust under seawater conditions presents its challenges. One of the major challenges faced in creating a robust thin-film sensor is the poor adhesion at the metal/polymer interface ^[88]. As the conductive metal layer and the polymer substrate are rather dissimilar materials, the cohesive energy of metals is typically two orders of magnitude higher than that of polymers ^[89]. The harsh conditions (i.e., high crossflow and high pressure) in the membrane pressure vessel would greatly escalate the susceptibility to failure due to delamination. In addition, seawater environments are highly corrosive for most metal-based (i.e., copper, silver, brass, zinc) electrodes/sensors. To overcome these challenges, the selection of functional material/ink and the development of sintering techniques are critical to creating reliable and functional printed electrodes for desalination application.

4. Printed electrodes for EIS

As the use of EIS for analytes detection becomes more mature, the design of the electrode has transformed from a simple cylindrical electrode design to a more complex planar microelectrode design such as the interdigitated electrodes and the microelectrodes arrays ^[22]. For decades, such complex planar microelectrode design is achieved by using conventional lithography, silicon chip, and cleanroom technologies which are often costly and time-consuming ^[23, 24]. Besides, the microelectrodes fabricated using this technology are often rigid and brittle as they are fabricated on silicon wafers as the substrate material. With the focus of the industry shifting towards the use of low-cost and high-throughput technology, the fabrication of electronic components including the electrodes using additive manufacturing approaches has been widely adopted ^[25]. Additive manufacturing of electronics or printed electronics is getting more attention because it provides numerous benefits such as (1) the ability to process a wide range of substrate materials including flexible materials and (2) shorter time for prototyping and fabrication process compared to the conventional method ^[26].

Printed electronics is a field of study that has gained much attention in the field of electronics fabrication, especially for flexible and wearable electronics. Printed electronics fabrication technology involves the deposition and patterning of functional inks onto a substrate in an additive manner to produce electronic components such as circuits, resistors, capacitors, inductors, transistors, as well as electrodes ^[25, 26]. With printed electronics technology, a wide range of nanomaterials such as gold nanoparticles, silver nanoparticles, carbon-based materials, and conducting organic materials can be

made into functional inks that are compatible with the printing techniques and printed directly onto a substrate to produce printed electrodes ^[21, 90]. The high-resolution printing capability and flexibility of the printing technology enables researchers to come up with more intricate and miniaturized electrode designs. Such features can bring advantages to the electroanalytical system in terms of speed, cost, portability, and solvent/sample consumption ^[20]. To date, printed electrodes have been utilized in a wide range of electrochemical sensing and biosensing applications such as the detection of ions, chemicals, DNAs, biomolecules, antigens, microorganisms, and enzymes ^[19].

4.1 Design of electrodes and electrode systems

Similar to other electrochemical techniques, EIS technique needs at least two electrodes to measure the impedance of the electrochemical cell, or more specifically the electrode-solution interface ^[91]. The design of the electrodes and the electrode configurations play crucial roles in determining the performance of the electrochemical cells. In general, there are three different types of electrode configurations, which are the two-electrode system, three-electrode system, and four-electrode system (Figure 3). Among these electrode configurations, the two-electrode system and three-electrode system are most utilized for the detection of analytes using EIS.

(a) two-electrode system (b) three-electrode system (c) four-electrode system

Figure 3. Schematics showing different electrode systems, namely (a) two-electrode system, (b) three-electrode system, and (c) four-electrode system. SUT represents sample under test. [Reprinted with permission from ref ^[92]. Copyright 2017 IOP publishing]

4.1.1 Two-electrode system

In a two-electrode system, a working electrode and a counter electrode are used to form a complete electrochemical cell with the analyte solution ^[91]. The adsorption of analytes on the surface of working electrodes can result in an interfacial impedance which can be detected using EIS. For better detection

of analytes, the impedance of the electrodes must be lower than the impedance at the electrode-solution interface ^[46]. The impedance can be lowered by (1) increasing the surface area of the electrode and (2) avoiding the adsorption of unwanted substances on the working electrode ^[46, 93]. For instance, the surface area of the counter electrode is normally ten times larger than the working electrodes to reduce the contribution of the impedance of the counter electrode to the entire circuit (Figure 4a) ^[46]. For surface-modified working electrode, a binding event can be traced by observing (1) the change in resistance when a redox-active compound is added to the solution, or (2) the change in capacitance when the redox-active compound is omitted ^[46]. In certain instances, the impedance can be determined at the "open circuit" potential (OCP) when the situation is equilibrated at the electrode influenced by the solution composition ^[46]. In such cases, a simple two-electrode arrangement may reasonably be utilized if the condition is stable during measurement. Alternatively, a bias potential is normally applied to the working electrode with respect to the open circuit potential to define a condition or force a process to occur (i.e. oxidation process) ^[46]. A potential is generated at the working electrode-solution interfaces when the analyte solution comes in contact with the electrodes ^[91]. The magnitude of the potential is influenced by the electrode microstructure, surface composition, and ionic strength of the solution. However, it is hard to precisely determine the working electrode potential because it relies on the oxidation potential of the redox species used. This is normally overcome by using a three-electrode system because the additional reference electrode allows for precise control over the bias potential applied at the working electrode-solution interface ^[46]. Besides, the two-electrode system normally suffers from poor temporal instability and reproducibility ^[94]. Therefore, researchers have shifted their attention to enhancing the quality of surface functionalization layers to unravel the time drift issue ^[94]. Despite the disadvantages, two-electrode system are still frequently used because of its simplicity in design and amenability to miniaturization ^[91].

The two-electrode system often uses electrodes with similar materials. A common example is interdigitated electrodes (IDE). Generally, IDEs comprise equal pairs of working and counter electrodes with interdigitated fingers and are separated by an insulating material (figure 4b) ^[95]. The typical IDE design parameters and schematics of the IDEs equivalent electrical elements and the model of the equivalent circuit are shown in figure 4c. IDEs have several benefits like low ohmic drop, quick response time, superior signal-to-noise ratio, utilization of low solution volumes, and fast kinetics of reaction ^[91]. This can be ascribed to the current flowing in close proximity to the surface due to the geometry of the IDEs, resulting in much higher sensitivity for detecting surface changes as compared to the conventional electrodes. The sensitivity of the electrodes can be improved by using a stronger

electric field, which can be achieved by reducing the gap width between the interdigitated fingers^[91]. A theoretical investigation has shown that 80% of the current flowing across the IDE electrodes with a gap width of 250 nm remains within 250 nm from the surface, thus improving the sensitivity of the binding event^[91]. This is usually limited by the resolution of the fabrication techniques. Often, the IDEs are fabricated using microfabrication^[96], screen printing^[93], gravure printing^[97], and inkjet printing technologies^[98]. The most found finger gap widths typically fall in the range of 1-150 μm . Although small finger gap width can result in higher sensitivity, a too-small finger gap width can result in short-circuiting, leading to an unmeaningful measurement^[91]. IDEs, however, can hardly be used in a three-electrode configuration because of the inaccessibility of the reference electrode from the current path between the pairs of working electrodes^[91]. In cases like measurement of a bulk sample where high penetration depth is preferred, the number of fingers of working electrodes between the counter electrodes can be increased to enhance the penetration depth of the fringing electric fields^[99]. It has been found that the optimum square IDE structure for maximum frequency range is $W = 1.5G$ and $L = (2.5N-1)G$, where W is the finger width, G is the gap width, L is the finger length, and N is the number of fingers^[92]. Besides, the electrodes can be made flexible by fabricating on a flexible substrate to make them conform to various shapes of the analytical devices (figure 4d)^[100].

Figure 4. Various two-electrode system designs. (a) A typical two-electrode system consisting of a large counter electrode and a smaller working electrode [Reprinted with permission from ref^[101]].

Copyright 2018 Elsevier], (b) A typical design of interdigitated electrode (IDE) [Reprinted with permission from ref^[98]. Copyright 2019 MPDI], (c) Schematic showing the design parameters of an IDE and its equivalent circuit [Reprinted with permission from ref^[92]. Copyright 2017 IOP Publishing], (d) A flexible impedance-based electrode fabricated on polyimide substrate for flexible application [Reprinted with permission from ref^[100]. Copyright 2020 IEEE].

4.1.2 Three-electrode system

In contrast, a three-electrode system consists of an additional reference electrode as compared to the two-electrode system. The reference electrode is used to apply a known potential difference between the working electrodes and the solution ^[91]. This improves control over the bias potential utilized at the working electrode-solution interface ^[91]. Ideally, the reference electrode should be positioned near to the working electrode and the current path between the working electrode and the counter electrode ^[91]. In general, there are several requirements for the reference electrodes, which are (1) they must have high current exchange density and non-polarizable, (2) the potential of the electrode must be reproducible, (3) the potential drift must be minimized during operation, and (4) they must be compatible with the working electrodes ^[102]. The miniaturization of reference electrodes needs to be done carefully as smaller electrodes tend to have reduced stability and lifetime due to the smaller surface area and volume as compared to the macro-sized reference electrodes ^[102].

Similar to the two-electrode system, the counter electrode can be made as large as possible to minimize its effect on the overall observed impedance (figure 5a) ^[91]. Unlike the two-electrode system, the three-electrode system tends to exhibit better temporal stability, shorter detection time, and minimal background effect ^[91, 94]. In a three-electrode system, the working electrode, counter electrode, and reference electrode are often made up of dissimilar materials. In most cases, the materials used for the reference electrode are either silver (Ag) ^[103, 104] or silver-silver chloride (Ag-AgCl) ^[4] because they are inexpensive, stable, and non-toxic. The counter electrodes are often made up of conducting materials with high conductivity such as gold ^[103] and silver ^[105]. Depending on the analytes, the working electrode can use either the same or different material from the counter electrodes. For instance, a gold working electrode is used for detecting dissolved oxygen, whereas a carbon electrode is used for detecting the pH of a solution ^[103]. For applications like membrane fouling detection, the working electrode can be the membrane filter with platinum wire and silver wire as counter and reference electrodes respectively ^[105]. Besides, three-electrode systems have also found applications in biosensor, neuromuscular cartography, and electrochemical cells (figure 5b, 5c, and 5d).

Figure 5. Various electrode designs for three-electrode configuration. (a) Typical screen-printed electrode design for heavy metal detection and chemical sensing [Reprinted with permission from ref^[4]. Copyright 2014 IEEE], (b) Miniaturised three-electrode biosensor [Reprinted with from permission ref^[94]. Copyright 2014 Elsevier], (c) Microelectrode arrays for neuromuscular cartography [Reprinted with permission from ref^[106]. Copyright 2016 Wiley Online], (d) 3D-printed electrochemical cells [Reprinted with permission from ref^[104]. Copyright 2018 Elsevier], where the counter and reference electrodes are represented in A.1 while the use of screen-printed electrode (SPE) in A.2 dispenses the use of external counter and reference electrodes.

4.1.3 Four-electrode system

A four-electrode system comprises a working electrode, working sense electrode, counter electrode, and reference electrode as shown in figure 6^[107]. Basically, a current is passed between the working electrode and the counter electrode. Additionally, a working sense electrode and a reference electrode are placed in between the working electrode and the counter electrode to measure the potential difference across the samples and hence the impedance^[108]. Although four-electrode system is less commonly used, it has found applications in protein detection (figure 6a)^[108], cell detection (figure 6b and 6c)^[109, 110], and membrane monitoring (figure 6d)^[111].

Figure 6. Various electrode designs of four-electrode configuration. (a) microband electrodes for τ protein detection [Reprinted with permission from ref^[108]. Copyright 2017 Elsevier], (b) Double interdigitated microelectrode for cell detection^[110], (c) chamber system with 4 embedded electrodes for cell detection [Reprinted with permission from ref^[109]. Copyright 2019 Infinite Science Publishing], (d) electrodes configuration for membrane characterization [Reprinted with permission from ref^[39]. Copyright 2012 Elsevier].

4.1.4 Design considerations for two-, three-, and four-electrode systems

It is important to take note of the geometry effect of the electrode such as the size, spacing, and distribution to ensure consistent and reproducible results regardless of the electrode system that is being used^[91, 112]. Also, the presence of artifacts of the respective electrode systems should also be taken into consideration when choosing the electrode systems.^[111, 113] In an electrochemical system, artifacts are distortion in the electrical impedance measurements. Artifacts are normally observed at high frequency when using a high impedance reference electrode. The electrode artifacts of a three-

electrode system can be minimized by (1) using a working electrode and counter electrode with similar impedance, (2) placing the reference electrode between the working electrode and counter electrode, (3) using a working electrode with a high double-layer capacitance than the stray capacitance, and (4) using identical cables with a short length and proper shielding ^[114]. In contrast, the electrode artifacts of a four-electrode system can be minimized by reducing the size of the reference and working sense electrode to avoid the distortion of the electric field ^[109].

4.1.5 Multi-layered electrode design

While the single-material electrodes are well suited for most applications, the performance of the electrodes can be enhanced by combining different materials, making use of the respective advantages from each material. For printed electrodes, this is often achieved by stacking one material over other materials resulting in a multi-layered electrode. For instance, a multi-layered silver/carbon electrode array with a top polyimide dielectric layer has been attempted in which the high conductivity silver serves as the feedline shut, whereas the nano-porous carbon serves to provide high interfacial capacitance for high signal-to-noise ratio sensing (figure 7a) ^[24]. In addition, a sensing layer that is sensitive to the target analyte can be placed on the IDEs for enhanced analyte detection. This multi-layered electrode design is more commonly known as the ion-selective electrode. For instance, Hibbard et al. have demonstrated that the addition of a layer of polyaniline nanoparticles layer on the silver IDEs for anomia gas detection (figure 7b) ^[50]. Sjöberg et al. have fabricated an ion sensor that has a K^+ -selective membrane and a non-selective membrane deposited on both the gold working and counter electrodes, respectively (figure 7c) ^[115]. Besides, it has been shown in many reports that electrodes can be coated with a thin layer of nanoparticles to enhance the sensitivity of the sensing electrode ^[116-118].

Figure 7. Various multi-layered electrode designs. (a) Multi-layered silver-carbon microelectrode arrays for bioelectronic device [Reprinted with permission from ref ^[24]. Copyright 2018 Wiley Online], (b) IDE electrode with a polyaniline layer for ammonia gas detection [Reprinted with permission from ref ^[50]. Copyright 2013 Elsevier], (c) Ion sensor with multi-layered electrode design [Reprinted with permission from ref ^[115]. Copyright 2016 Elsevier]

4.1.6 Microelectrode arrays (MEAs)

With proper fabrication techniques, the electrodes can be miniaturized and rearranged to form microelectrode arrays (MEAs) that can bring added advantages such as the increased spatial resolution, the ability to set up controls within the same experiment, and the ability to take multiple measurements at different sites in real-time ^[119]. Conventionally, MEAs for electrochemical applications can be fabricated using assembly technique, photolithography technique, and electrodeposition technique ^[119]. For instance, Xu et al. fabricated an MEA for water quality assessment that can detect dissolve oxygen, pH, temperature, and conductivity of the water in real time^[103]. Similarly, Schnitker et al. fabricated a 1cm x 1cm MEA packed with 60 silver/carbon composite electrodes that can be used for in-vitro cell detection (figure 8a) ^[24]. Besides, there have been several reports demonstrating the use of silicon chip technology for fabricating MEAs not only for detecting cells but also for imaging and locating cells using high-density arrays (figure 8b) ^[23, 120-122]. Several criteria have been identified for assessing the quality of the MEAs, which are (1) the number of electroactive electrodes, N , (2) the position and stability of the equilibrium potential, P_{eq} of the redox system, and (3) the uncompensated resistance, R_u ^[23]. P_{eq} provides information about the quality of the pseudo-reference electrodes, N determines the function of the MEAs, and R_u can affect the integration with the peripheral electronic components. The uncompensated resistance of an MEA normally dictates the relaxation time constants in electroanalytical investigations, thus it is preferable to have low R_u . EIS and cyclic voltammetry (CV) can be used simultaneously to provide information about the number of working electroactive electrodes in the MEA which can then be compared to the number of electrodes available on the MEA, thus indicating the quality of the MEA.

Figure 8. Various microelectrode array designs. (a) MEA with dissolved oxygen, pH, temperature, conductivity sensors for water quality assessment [Reprinted with permission from ref ^[103]. Copyright 2016 Elsevier], and (b) Complementary Metal Oxide Semiconductor (CMOS)-based microelectrode array for cell imaging application [Reprinted with permission from ref ^[121]. Copyright 2018 IEEE]

4.2 Methods of printing electrodes

To date, various additive manufacturing techniques such as gravure printing, screen printing, inkjet printing, and aerosol jet printing have been employed for the fabrication of electrodes. This section aims at discussing the state-of-the-art fabrication processes and their advantages and disadvantages for fabricating printed electrodes.

4.2.1 Screen printing

The screen printing technique is a contact printing technique that utilizes a stencil to mask out the unnecessary regions on the substrates for preventing the ink from coming in contact with the substrates, thus forming the patterned ink (figure 9a) ^[25]. A squeegee is used to spread the ink uniformly over the opening of the stencil for controlled ink deposition. A huge benefit of the screen-printing technique is that it allows the use of a wide range of substrates from rigid materials such as ceramics and glass to flexible materials such as papers, textiles, and polymer membranes ^[26]. In addition, screen printing technique allows for thick film fabrication where it can be useful for fabricating high conductivity electrodes through thickening the electrode's conductive layers ^[19]. Not only does the process offers huge design flexibility, but it is also fast, highly repeatable, highly automated, and suitable for large-area electronics fabrication ^[19]. Besides, surface modification can be done easily to the screen-printed electrode to improve the selectivity and sensitivity for detecting different analytes ^[3].

A major disadvantage of screen printing comes from the use of highly viscous inks which typically exist in paste-like form. The inks are made viscous to avoid the unintentional spreading of ink ^[123]. This is achieved by adding organic binders to the ink to increase its viscosity. However, it often results in a material with an electrical conductivity lower than the conductivity of the bulk material ^[123]. This can be compensated by fabricating a thicker electrode and using proper sintering steps. Nevertheless, the thick film with a high surface roughness of screen-printed electrodes is less ideal for microfluidic devices that require a flat and smooth surface ^[102, 124].

To date, various materials such as gold ^[125, 126], silver ^[127, 128], carbon ^[129, 130] have been attempted for the fabrication of printed electrodes ^[21]. Besides, screen printing technique is also suitable for fabricating multi-layered electrodes of different materials ^[4]. Printing of various electrode designs such as IDEs ^[131], three-electrode systems with multi-layered electrode design ^[132], and microelectrode arrays ^[133] using screen printing technique has been successfully demonstrated.

4.2.2 Gravure printing

Gravure printing technique is a contact printing technique that is compatible with the high throughput roll-to-roll (R2R) fabrication technique for the mass production of thin-film electronics. The gravure printing technique normally comprises four fundamental components, which are an ink bath, a gravure cylinder, a doctor blade, and an impression blade (figure 9b) ^[26]. The gravure cylinder contains the grooves of the desired patterns engraved on its surface. The doctor blade is used to get rid of excess ink from the gravure cylinder leaving behind the ink in the grooves. The impression cylinder is used to press the continuous roll of the flexible substrate against the gravure cylinder to transfer the ink from the gravure cylinder to the substrate ^[134].

Unlike other printing techniques, gravure printing can achieve an ink pattern with varying ink film thicknesses in a single print which can significantly enhance the production efficiency when such electrode design is necessary ^[135]. Compared to the screen printing technique, gravure printing uses less viscous ink which is beneficial in terms of the conductivity of the ink. In most cases, silver nanoparticle ink and polyethylene terephthalate (PET) substrate have been utilized for printing electrodes using gravure printing ^[136, 137].

Till now, gravure printing technique has been used to fabricate electrodes such as the IDEs ^[136, 137], various three-electrode systems ^[136], and multi-layered electrode design ^[138]. Detection of various analytes such as cadmium sulphide (CdS), lead sulphide (PbS), D-proline, and mouse immunoglobulin G (IgG) have been successfully demonstrated ^[137].

4.2.3 Inkjet printing

Inkjet printing is a non-contact printing technique where the inks are deposited onto a substrate through a digitally controlled nozzle in an additive manner (figure 9c) ^[25]. Generally, inkjet printing techniques can be categorized into 2 groups, which are continuous inkjet printing and drop-on-demand inkjet printing ^[26]. The continuous inkjet printing technique, literally, suggests that the droplets of ink coming out from the nozzles are continuous. In order to control the deposition of ink, the ejected droplets of ink at the non-print regions are normally electrically charged and deflected into a gutter by applying an electric field. Drop-on-demand inkjet printing, on the other hand, controls the deposition of ink using several actuation methods such as thermal, piezoelectric, and electrostatic actuations.

Inkjet printing technique is advantageous in several ways, (1) cost-saving as materials are deposited at required areas, (2) the non-contact process avoids cross-contamination of inks, and (3) high design flexibility and short prototyping time ^[26]. However, inkjet printing has several downsides such as (1) the nozzle is easily clogged, (2) the ink requirement is very high as it is only suitable for a small viscosity range, and (3) it can only be used for fabricating electrodes with planar design ^[26].

A wide variety of inks such as gold nanoparticle ink ^[115], silver nanoparticle ink ^[139], carbon ink ^[24], just to name a few, have been demonstrated using inkjet printing. Inkjet printing process is highly suitable for the fabrication of electrode design with small feature sizes such as interdigitated electrode ^[98] and microelectrode arrays due to its high-resolution printing capability ^[24]. Besides, it can also be used for printing multiple-materials electrode designs. In addition, inkjet printing process is compatible with numerous types of substrates such as glass, silicon wafer, and many other polymeric materials ^[140]. As such, inkjet printing has been widely used to fabricate flexible electrodes for a wide variety of flexible electrochemical applications ^[140].

4.2.4 Aerosol jet printing

Aerosol jet printing is a non-contact printing technique in which the droplets of ink are deposited onto a substrate through an aerodynamic-focusing technique to form a tiny stream of inks that exits the nozzle at high velocity (figure 9d) ^[141]. In the beginning, the ink is first atomized by using either a pneumatic atomizer or an ultrasonic atomizer. The droplets of ink are then delivered to the deposition head via a delivery tubing. At the deposition head, the droplets of ink are then focused by an annular sheath flow and exit through a nozzle ^[142]. The high exit velocity allows the ink droplets to travel a long distance without any change in trajectory, allowing for a large stand-off distance printing. This allows aerosol jet printing to have great tolerance to the irregularity of the substrate surface. In addition to the capability of utilizing various functional inks, a wide range of substrate materials can also be used

in the aerosol jet printing process^[143, 144]. Besides, it has been shown in many reports that the print resolution of aerosol jet printing can be as low as ten μm , allowing for the production of electrodes with small and intricate features^[145-147]. Most importantly, the 5-axis motion controller allows the printhead to move arbitrarily in any position and orientation, opening the opportunity for conformal printing of electrodes on various complex surfaces^[148]. However, the print speed of aerosol jet printing is relatively slower than the aforementioned printing techniques due to the single-printhead configuration. Besides, it is essential to make sure the particle size in the ink is less than the typical aerosol diameter of 1-5 μm to ensure good printability of the functional material^[142]. Also, aerosol jet printing suffers from system drift issues where the quality of the printed devices would vary from time to time resulting in devices with inconsistent performance^[149]. Despite the limitations, aerosol jet printing offers great design flexibility to electronics designers, making it suitable for the production of highly customized electronic components such as electrodes. Although not many works on the fabrication of electrodes using aerosol jet printing have been reported, printed interdigitated electrodes^[150] and microelectrode arrays^[151] are some of the few that have been successfully demonstrated using aerosol jet printing.

Figure 9. Schematic showing different fully additive printing processes, namely (a) screen printing process [Reprinted with permission from ref^[152]. Copyright 2017 Royal Society of Chemistry]., (b)

gravure printing process, (c) inkjet printing process, and (d) aerosol jet printing process. [Reprinted with permission from ref^[153]. Copyright 2017 IOP Publishing]

In brief, each printing technology has different advantages that can be utilized by electrode designers for producing electrodes. Table 1 summarizes and compares the key features of the printing techniques such as the minimum printable feature size, ink viscosity, print speed, layer thickness, and the advantages and disadvantages. Generally, all print techniques can produce a reasonably small feature size owing to the high-resolution printing capability. The selection of the fabrication techniques can be recommended based on the needs, whether it is for mass production of electrodes or fabrication of highly customized electrodes. For the former, screen printing and gravure printing techniques are recommended due to the R2R fabrication compatibility, whereas inkjet printing and aerosol jet printing are recommended for the latter.

Table 1. Comparison among the fully additive printing techniques in terms of the feature size, ink viscosity, print speed, layer thickness, advantages, and disadvantages. (Adapted from Ref ^[26])

Printing techniques	Minimum feature size (μm)	Ink viscosity (cP)	Print speed (m/min)	Layer thickness (μm)	Advantages	Disadvantages
Screen printing	30-50	1000-50000	10-15	Up to 12	<ul style="list-style-type: none"> • Compatible with R2R fabrication • Wide material choice • Thick film fabrication 	<ul style="list-style-type: none"> • Require a stencil which makes it costly for prototyping • Limited to planar design • High surface roughness
Gravure printing	10-50	50-200	100-1000	0.8-8	<ul style="list-style-type: none"> • Compatible with R2R fabrication • Wide material choice • Can produce electrode film with varying thickness 	<ul style="list-style-type: none"> • Require a gravure cylinder which makes it costly for prototyping • Limited to planar design
Inkjet printing	30-50	5-20	15-500	<0.5	<ul style="list-style-type: none"> • High design flexibility 	<ul style="list-style-type: none"> • Strict ink requirement • Limited to planar design • Partially compatible with R2R fabrication
Aerosol jet printing	~10	1-5 (UA) 1-1000 (PA)	Up to 12	0.1-2	<ul style="list-style-type: none"> • High design flexibility • Conformal printing of electrodes on curve surfaces • High resolution 	<ul style="list-style-type: none"> • Partially compatible with R2R fabrication • Low print speed

4.3 Materials for printed electrodes

Material selection for the electrochemical electrodes is an important aspect when designing the electroanalytical device as it dictates the device's performance. Various materials such as noble metal nanoparticles, carbon-based nanomaterials, organic materials, and nanocellulose materials have been utilized and made into functional inks for the fabrication of printed electrochemical electrodes, which will be discussed in detail in the following sections.

In general, these materials are usually made into inks that are compatible with the printing techniques used. The inks typically consist of functional materials, stabilizing agents, solvents, and additives (Figure 10) ^[154]. The functional materials that are used for printing electrodes are normally in the form of nanomaterials because they can form a nanostructured surface that can enhance the sensitivity, selectivity, and stability of the electrode. Besides, these nanomaterials such as nanoparticles, nanotubes, and nanoflakes often form porous structures that possess a large surface area for adsorption and reaction which improves the sensitivity of the electrodes ^[24, 146, 155, 156]. It should be highlighted that the porosity of the metal nanoparticle film strongly depends on the sintering condition ^[156]. The functional materials are normally carried and dispersed in a solvent and a stabilizing agent is normally added to impede the aggregations of nanomaterials and to slow down the oxidation of the nanomaterials (if any, e.g. metal nanoparticles). Post-processing treatments such as heat, ultraviolet, or photonic sintering are needed to remove the electrically insulating organic stabilizer. The additives such as dispersants, wetting agents, and binding agents are added to the inks to enhance the suspension homogeneity and compatibility of the ink to the substrates and the printing techniques ^[157]. The final electrical property depends on several factors such as the type of functional material, ink loading, sintering techniques used, and the final deposition pattern of the ink which is dictated by evaporation mode and particle-substrate interactions ^[145, 158].

Figure 10. Different components of functional inks

4.3.1 Noble metal nanomaterials

Noble metals refer to metals that are highly resistant to oxidations and chemical reactions. Noble metal nanomaterials such as gold, silver, platinum, and palladium are commonly used for fabricating

electrochemical electrodes due to their inertness and high conductivity. Another reason is that metal nanomaterials have much lower melting points as compared to their bulk counterparts, thus making them compatible with a wider range of substrates besides saving energy. Furthermore, the electrocatalytic property of these noble metals makes them suitable to be used for electrochemical electrodes. Noble metal nanoparticles are normally utilized for the fabrication of enzyme-free electrochemical electrodes because they are more stable and reproducible for peroxide detection ^[159].

Gold nanoparticle ink is the most commonly used electrode material in a wide variety of electrochemical applications due to its good thermal stability, oxidation stability, and electrical conductivity ^[90, 160]. The electrical resistivity of gold nanoparticle inks typically falls in the range of $8.7 \times 10^{-8} - 7.5 \times 10^{-7} \Omega \cdot m$ depending on the sintering conditions ^[160, 161]. The high electrical conductivity reduces the contribution of the impedance of the electrodes to the overall impedance of the electrochemical system, thus enhancing the detection sensitivity. Besides, gold nanoparticle ink is highly resistant to oxidation which makes it suitable for applications that require a long lifetime such as wearable devices, which may encounter high salt concentration from sweat ^[160]. In terms of electrode fabrication, screen printing and inkjet printing are the more popular printing techniques that have been utilized for the fabrication of electrodes such as the interdigitated electrodes and microelectrode arrays ^[125, 160]. However, gold nanoparticle ink is relatively costly making it unsuitable for low-cost electronic applications and it tends to have a melting temperature of greater than 190 °C, thus restricting the choice of substrate materials that can be used ^[160]. Often with EIS, the surface of gold electrodes in the biosensors are usually modified with enzymes ^[162], antibody ^[163], and oligonucleotide ^[164] for detection of protein ^[165], antigen ^[166], and DNA ^[167], just to name a few ^[168].

Silver nanoparticle ink, on the other hand, is less expensive compared to gold nanoparticle ink which makes them more suitable for low-cost electronic devices. Although silver has higher bulk resistivity compared to gold, the resistivity of the silver nanoparticle ink typically ranges from $4.0 - 5.6 \times 10^{-8} \Omega \cdot m$ which is lower than gold nanoparticle, making them a better candidate for low impedance printed electrodes ^[156, 169]. In addition to the low sintering temperature which typically ranges from 110 – 200 °C ^[170], silver nanoparticle inks are found to be compatible with a wide variety of sintering techniques such as chemical ^[171], photonic ^[172], laser ^[173], and electrical ^[174] sintering. However, silver nanoparticle inks tend to have lower oxidation resistance compared to other noble metal nanoparticle inks, thus less suitable for long lifetime applications ^[175]. It has been found that electrodes made up of silver nanoparticles have a lifetime of around a week before they are oxidized ^[159]. This can be solved by (1) coating a layer of passivation layers over the surface of the silver electrode if adsorption of analytes is not necessary or (2) replacing the oxidized silver nanoparticle electrodes with new electrodes since

the material cost is low. To date, printed electrodes made of silver nanoparticle inks have been used for the detection of peroxide^[159], ampicillin^[139], and ammonia^[176].

Palladium nanoparticle ink is getting more attention to be used as sensing electrodes due to its unique electrocatalytic properties^[90]. Also, palladium nanoparticles were used to catalyze the oxidation of small organic molecules such as ethanol and formaldehyde, making them a suitable material for beer sensors and formaldehyde sensors^[159]. However, there are only a handful of reports on the printing of electrochemical sensing electrodes using pure palladium inks^[177]. Qin et al. have demonstrated inkjet printing of a pH sensor using high loading palladium ink for the sensing electrodes^[177]. The reported resistivity of the palladium nanoparticle inks is 2.6 $\mu\Omega\cdot\text{m}$. More commonly, the palladium nanoparticles are used in conjunction with other materials such as carbon-based inks^[178, 179] as a composite electrode for enhanced sensitivity and selectivity. For instance, screen-printed electrodes with palladium nanoparticles and carbon have been used for monitoring glucose^[159].

Platinum electrode is widely used as the non-enzymatic electrode for the detection of molecules in household goods such as cosmetics, food, and beverages due to the high electrocatalytic activity towards peroxide^[159]. Goldie et al. have demonstrated the printing of platinum nanoparticle ink using inkjet printing and achieved an electrical resistivity of $2.5 \times 10^{-7} \Omega\cdot\text{m}$, which is approximately 4 times higher than the bulk platinum^[180]. However, there is no report on the printing of platinum electrochemical electrodes using platinum nanoparticle inks to the best of the authors' knowledge. Instead, platinum nanoparticles are more commonly applied to screen-printed carbon electrodes using electrochemical deposition to enhance the detection of peroxide^[181, 182].

4.3.2 Carbon-based materials

Carbon ink in the form of a mixture of graphite powder and pasting liquid is widely used for the fabrication of screen-printed carbon electrodes for many years due to its good conductivity and low material cost^[93, 130, 183-186]. However, the focus has shifted towards finding alternative carbon nanomaterials for improved electrode performance and better compatibility with other printing techniques. Carbon-based nanomaterials or carbonaceous nanomaterials such as graphite, carbon black, carbon nanotubes, and graphene are getting more popular for electrochemical applications due to their superior electrocatalytic property. Compared to the noble metal nanomaterials, carbon-based nanomaterials are relatively inexpensive and possess fair electrical conductivity which is beneficial for producing low-cost electrochemical electrodes.

Over the past few years, carbon nanotubes have become a popular electrode material due to their extraordinary properties such as high conductivity and mechanical flexibility^[145, 187, 188]. Unlike metal

nanoparticle electrodes which are costly and require high sintering temperature, carbon nanotubes are cheap and readily conductive, eliminating the need for a sintering process^[189]. The low processing temperature of carbon nanotubes also makes them a potential candidate for roll-to-roll fabrication of flexible electrochemical devices^[137]. In terms of electrochemical sensing, carbon nanotubes have benefits such as improving the electrocatalytic properties which significantly reduce the overpotential, enhancing the current of redox systems, boosting the reaction rate and the electrode kinetics, and improving the stability and reproducibility of the electrode's response^[190, 191]. A study has shown that carbon nanotube (CNT) electrodes demonstrate better sensitivity and lower detection limits compared to traditional electrodes^[191]. Another advantage of CNTs is the ability to be chemically modified with different functionalization groups at their sidewalls for detecting specific analytes. Also, the surface of the CNTs can be decorated with noble metal nanomaterials to improve the selectivity and sensitivity of the electrodes. Randviir et al. used screen printing technology to modify the surface of graphite working electrodes with multi-walled carbon nanotubes for the detection of capsaicin^[192].

Carbon black is carbon nanoparticles with sizes ranging from 20 to hundreds of nm^[190]. Since the discovery of the use of edge-plane-like defects of CNTs for electrochemical detection of analytes, many researchers have attempted using carbon black, which possesses a high number of defect sites, as electrode material for enhanced analytes detection^[193, 194]. The main application of carbon black is for the activation of the surface of electrodes^[190]. In the early research, carbon black modified-SPE has been found useful for the detection of analytes in the gaseous phase and the fuel cells^[195, 196]. Following that, carbon black electrodes have been used in numerous applications for detecting analytes in solutions^[194, 197, 198]. Also, carbon black electrodes can be used as biosensors^[199]. Compared to carbon nanotubes, the main advantage of carbon black is its lower cost, making it widely adopted for various industrial applications^[190]. Despite the use of inkjet printing for the fabrication of carbon black electrode^[200, 201], there is no reported work on using fully printed carbon black electrode for analyte detection.

Graphene has a 2-dimensional molecular structure with a single layer of carbon atoms that are covalently bonded together. The sp² hybridization of electron orbitals among carbon atoms allows the electrons to flow freely across the molecular structure. The unique properties of graphene such as high mechanical flexibility, electrical and thermal conductivities, chemical resistance, and biocompatibility have enabled many electrochemical applications such as electrodes for batteries and wearable devices^[202-204]. The electrocatalytic property of graphene can be attributed to the structural defects, the large number of edge-plane sites, and the presence of the functionalization groups^[190]. Typically, graphene inks are electrochemically synthesized via the reduction of graphene oxide,

therefore it is also known as reduced graphene oxide. The reduced graphene oxide normally contains some remaining carboxyl or hydroxyl groups from graphene oxide that can be chemically modified with amine group ^[132]. With the amine group, the reduced graphene oxide can then be modified with numerous species such as proteins, nucleic acids, and nanoparticles ^[132, 205-207]. Parate et al. have successfully demonstrated antigen detection using a fully printed graphene-based IDE fabricated using aerosol jet printing technique ^[150].

4.3.3 Conductive polymers

Conductive polymers, organic polymers that conduct electricity, have gained popularity in applications like electromagnetic shielding, antistatic coating material, electroluminescent displays as well as electrochemical electrodes ^[208-210]. Among the conductive polymer, polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) are the more popular candidates as electrode materials for electrochemical applications.

The advent of aqueous PANI dispersion has widened the processability of PANI and opened up new applications such as organic electrochemical electrodes ^[211]. Since then, ink formulations of PANI for various types of printing techniques such as gravure printing ^[212] and inkjet printing ^[213, 214] have been developed. Typically, PANI-based sensors often come with (1) a multi-layered electrode design with a top PANI layer and a bottom IDE layer ^[50, 176, 215], (2) PANI-coated electrode ^[216], or (3) a PANI working electrode in a three-electrode system ^[217]. PANI has been used widely for gas detection such as ammonia and hydrogen sulphide ^[50, 176, 218]. In addition, PANI can also be used for detecting inorganic mercury ^[216] and DNA, via the sensing of hydronium ion, a by-product of DNA amplification reaction ^[217].

PEDOT:PSS is the most frequently used PEDOT derivatives because the PSS prevents the PEDOT from getting oxidized while maintaining the solution stability ^[219]. To date, the electrochemical electrode made up of PEDOT:PSS has been fabricated mostly using screen printing ^[219] and inkjet printing ^[220]. For electrochemical detection, PEDOT:PSS is often mixed with other substances such as PANI and graphene for improved sensitivity and selectivity ^[220, 221]. For instance, PANI/PEDOT:PSS composite conductive electrode is used for pH and humidity detection ^[222, 223]. Also, PEDOT:PSS is often combined with reduced graphene oxide as composite electrode materials for applications such as the detection of ammonia gas ^[220]. A disadvantage of aqueous PEDOT:PSS ink is that the adhesion of the substrates is often poor, thus resulting in limited applications of PEDOT:PSS ink for fabricating electrochemical electrodes ^[224]. PEDOT:PSS is found useful as the electrode material of bioelectronic interface for electrocardiograph (ECG) and its use for characterizing the skin-electrode impedance correlation using EIS ^[225].

Table 2 summarises some of the work related to the use of printed electrodes for EIS analysis. The table categorizes the printed electrode based on the materials of the working electrodes and shows other information such as the type of analytes, electrode design, printing method used as well as the electrode performance.

Table 2. Use of printed electrodes for different sensing applications.

Materials of working electrodes [Source of material]	Analytes	Electrode design	Printing methods [Model/ source of equipment]	Electrode performance	Ref.
Gold [Ercon Inc. (MA, USA)]	unmodified amplicons	Three-electrode design <ul style="list-style-type: none"> • Working electrode: Gold modified with oligonucleotide • Reference electrode: Ag/AgCl • Counter electrode: carbon 	Screen printing [DEK 248, (DEK, Weymouth, UK)]	<ul style="list-style-type: none"> • Linear range: 12 pmol/L – 12 nmol/L • Sensitivity: 52 kΩ/(nmol/L) • Detection limit: 1.2 pmol/L 	[162]
	[Dropsens] Protein	Three-electrode design <ul style="list-style-type: none"> • Working electrode: Gold modified with antibody • Reference electrode: Ag • Counter electrode: Gold 	Screen printing	<ul style="list-style-type: none"> • Linear range: down to 3.5 µg/mL • Sensitivity: 527 Ω/(g/mL) • Detection limit: 1.5 µg/mL 	[165]
Silver [Mitsubishi Imaging Inc.]	ampicillin	Aptamer-functionalized interdigitated electrode	Inkjet printing [Epson ET-2550]	<ul style="list-style-type: none"> • Linear range: 100 – 10,000 µg/mL • Detection limit: 10 µg/mL • Response time: 6 minutes 	[139]
	ammonia	Ion-selective electrode with silver interdigitated electrodes and PANI sensing layer	Inkjet printing [Epson C46/C48 piezoelectric printers]	<ul style="list-style-type: none"> • Linear range: 0-100 mg/L • Sensitivity: 2.1 kΩ/(mg/L) • Detection limit: <25 mg/L 	[176]
Carbon [GSI Technologies (Burr Ridge, IL, USA)]	bull serum albumin (BSA)	Three-electrode design All carbon electrodes design	Screen printing	<ul style="list-style-type: none"> • Linear range: 0-100 µg/mL • Normalized Sensitivity: 0.0472 (µg/mL)⁻¹ • Detection limit: 1.78 µg/ml 	[226]
CNT [Southwest Nanotechnologies, USA]	capsaicin	Three-electrode design <ul style="list-style-type: none"> • Working electrode: Multi-walled CNT • Reference electrode: Ag/AgCl • Counter electrode: graphite 	Screen printing [(DEK, Weymouth, UK)]	<ul style="list-style-type: none"> • Linear range: 0-4.0 mM • Sensitivity: 7.51 Ω/mM • Detection limit: 0.22 mM 	[192]
Graphene [Asbury, NJ, USA]	Antigens(IFN-γ)	Interdigitated electrode modified with anti-bovine	Aerosol jet printing [Optomec, US]	<ul style="list-style-type: none"> • Linear range: 0.1-5 ng/mL • Sensitivity: 44.9% per decade • Detection limit: 25 pg/mL 	[150]

Polyaniline	Ammonia gas	Ion-selective electrode with interdigitated electrodes and PANI sensing layer	Inkjet printing (polyaniline) and screen printing (silver)	<ul style="list-style-type: none"> • Linear range: 40–2175 ppbv • Normalized sensitivity: 0.0079 ppbv⁻¹ • Detection limit: 6.2 ppbv 	[50]
PEDOT:PSS [Heraeus, Clevios PH1000]	Bioelectronic interface	Single-electrode design	Inkjet printing [Dimatix DMP-2800, Fujifilm, US]	<ul style="list-style-type: none"> • Signal-to-noise ratio: 12 dB 	[225]

5. Conclusions and prospects

Printed electrodes are electrodes that are fabricated using printing techniques such as screen printing, gravure printing, inkjet printing, and aerosol jet printing in which the conducting materials are added onto a substrate according to the desired electrode designs. These printing techniques allow a wide range of conductive inks for the electrode materials to be used and the use of various types of substrate materials, thus realizing metallization of the surface of non-conducting materials.

Printed electrodes have been proven to be well suited for electrochemical impedance spectroscopy and show great potential in the field of membrane fouling detection. With these advanced printing tools that allow for more design freedom, researchers and electrode designers will be able to come up with new electrode designs with higher detection sensitivity and overcome some of the existing design and manufacturing challenges when using conventional fabrication methods.

While the use of printed electrodes for electrochemical impedance spectroscopy is not as widely adopted as compared to the other electrochemical methods such as cyclic voltammetry, they are expected to rapidly rise in popularity especially in the field of biosensing and membrane fouling detection due to the high customizability of electrodes. With tool-free printing technologies like inkjet printing and aerosol jet printing, customization of electrodes for dedicated applications is made possible at a much lower fabrication cost.

While existing printing technology can meet the requirements of printed electrodes for most EIS applications, challenges remain in obtaining electrodes with high electrical conductivity, high print quality, and good adhesion strength in certain cases, especially when dealing with substrate materials with high surface roughness, highly porous, and low thermal resistance. This is especially true for the RO membrane for water filtration treatment. Such substrate materials often limit the sintering temperature that can be used for sintering the conductive inks, resulting in printed electrodes with high electrical resistivity. As such, more efforts need to be made in search of new inks that can be sintered at much lower temperatures to unleash the potential of printed electrodes for a wider range of applications.

Acknowledgment

This research is supported by PUB, Singapore's National Water Agency under its Urban Solutions & Sustainability (Competitive Research Programme (CRP)(Water) Scheme, PUB-1804-0075) and the National Research Foundation, Prime Minister's Office, Singapore under its Medium-Sized Centre funding scheme.

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