Electrochemical Reactions in Pulsed Electric Fields Treatment

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Nomenclature

A	*Electrode area* [m^{-2}]
C_{dl}	Electronic double-layer capacitance [F]
E	Electric field strength [V m^{-1}]
E°_{red}	Standard reduction potential [V]
F	Faraday constant [C mol^{-1}]
f	Pulse repetition frequency [Hz]
F_v	Volumetric flow rate [m^3 s^{-1}]
i	Current intensity [A]
i_f	Faradaic current [A]
i_c	Non-Faradaic charging current [A]
$\boldsymbol{j}$	Current density vector
j	Current density [A m^{-2}]
i_f	FARADAIC current [A]
i_c	Non-Faradaic charging current [A]
$\boldsymbol{j}$	Current density vector
j	Current density [A m^{-2}]
m_{rs}	Amount of species s produced by the reaction r [g]
M_s	Molecular weight of the species s [g mol^{-1}]
n_p	Number of pulses [−]
n_{rs}	Number of electrons transferred for each product s formed by the reaction r [−]
Q_p	Total charge transferred per each pulse [C]
Q_r	Cumulative electric charge transferred by the reaction r [C]
Q_{tot}	Total transferred charge [C]
R_s	Resistance of the electrolytic solution [Ω]

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t_r	Residence time [s]
U	Electric potential [V]
U_{th}	Reaction potential [V]
v	Treatment volume [m^3]
W_p	Specific energy per pulse [kJ $\mathrm{kg}^{-1}\mathrm{pulse}^{-1}$]
W_T	Total specific energy [kJ/kg]
x_{dl}	Thickeners of the double layer [m]
Z_f	Faradaic impedance [Ω]

Greek Letters

σ	Electrical conductivity [S m^{-1}]
τ	Pulse width [s]
$\Delta\phi_{\mathrm{dl}}$	Potential drop across the electronic double layer [V]

Operators

Δ	Difference

Introduction

Pulsed electric fields (PEF) is an innovative nonthermal technology which has attracted considerable interest in the last decades in food industry due to its potential to provide the food processor with the opportunity to produce new and value-added food products and ingredients with reduced energy consumption and enhanced quality attributes preferred by consumers.

In PEF processing, a food product is physically and electrically contacted with the metal electrodes of a treatment chamber, operated either in batch-wise or in continuous, and exposed to repetitive (Hz-kHz) very short (μs-ms) electric field (E) pulses of low ($E < 2$ kV/cm), moderate ($E = 1$–5 kV/cm), or high intensity ($E = 10$–40 kV/cm) and relatively low energy input ($W_T = 0.1$–150 kJ/kg) supplied by a pulse generator. The pulse shapes commonly used in PEF treatments are either exponential or square-wave pulses, monopolar, or bipolar (Raso et al. 2016).

The application of electric pulses may cause either temporary or permanent formation of pores in the membranes of microbial, plant, or animal cells, referred to as electroporation or electropermeabilization, which disturbs and damages membrane's functionality (Kotnik et al. 2012), as well as induces targeted structural modification in the food matrix (Soliva-Fortuny et al. 2009).

This make PEF technology suitable for a wide range of applications in food industry, such as those involving the inactivation of microbial cells in liquid foods (e.g., pasteurization) (Saldaña et al. 2014), or mass transport phenomena of juice, water, and bioactive compounds from plant sources (e.g., extraction, expression, drying, osmotic dehydration, freeze-drying, freezing, freeze-thawing) (Bobinaitė et al. 2015; Donsì et al. 2010; Jalte et al. 2009; Parniakov et al. 2015, 2016a, b; Pataro et al. 2020; Wiktor et al. 2013), or requiring structural modifications to facilitate some unit operation of food processing (e.g., peeling, cutting) (Arnal et al. 2018; Soliva-Fortuny et al. 2009)..

With regard to these applications, PEF processing is particularly interesting due to its relatively low energy consumption and processing temperature, easy scale-up, and implementation into existing processing line due to its continuous flow operability with very short processing time. This has led, today, to the first industrial applications especially in the potato processing industry, where the PEF is operated at low field strength and energy input ($E < 2$ kV/cm, $W_T = 0.1$–2 kJ/kg) to facilitate cutting operations providing the highest potential in terms of technical feasibility as well as economical relevance (Fauster et al., 2018). On the other hand, only very few commercial-scale operations have been achieved for applications requiring high field strength and energy input ($E > 10$ kV/cm, $W_T = 50$–150 kJ/kg), as reported for pasteurization of liquid food such as fruit juices and smoothies (Kempkes 2017). In this case, several technological issues mainly related to the long-term reliability of PEF generator and electrodes as well as high investment, service and maintenance costs, consumers' acceptance, regulatory aspects, and toxicity risks still remain and have to be addressed prior to the full exploitation of PEF technology.

Most of these limitations are related to the unavoidable occurrence of electrophoresis and electrochemical reactions accompanying the flow of electric current through the PEF treatment chamber when typical conditions for PEF processing are applied. These reactions, especially those leading to corrosion and fouling of the electrodes, electrolysis of water, migration of electrode material, and chemical changes that may occur into the food product undergoing a PEF treatment, are undesired and must be minimized since these may seriously affect food safety (other than microbial) and quality, as well as process efficiency, equipment reliability, and cost aspects.

For these reasons electrochemical reactions have found increasing attention within the last years since their occurrence obviously raises concerns about PEF commercialization.

Historical Background

Electrically driven electrochemical reactions were first reported at the end of the nineteenth century, when it was found that the bactericidal effect of direct or low-frequency alternating current resulted from thermal and electrochemical effects (Prochownick and Spaeth 1890; Krüger 1893; Thiele and Wolf 1899).

In the 1920s a process called "Electropure" was introduced in Europe and USA (Beattie and Lewis 1925; Fetterman 1928), as the first attempts to use electricity for milk pasteurization. The process was performed by pumping the milk through a carbon electrode treatment chamber connected to a (not pulsed) 220 V alternating current source. Apart from thermal effects based on the mechanism of ohmic heating, lethal effects of electrochemical reactions such as the hydrolysis of chlorine were found when the applied voltage used to treat food was 3000–4000 V (Pareilleux and Sicard 1970).

A further attempt to use electricity to kill microorganisms was performed in the 1950s in a process called electrohydraulic treatment, which consisted in a rapid discharge of high-voltage electricity (electric arcs) across two electrodes submerged in the liquid medium containing the microorganisms (Gilliland and Speck 1967). Electrochemical reactions (electrolysis of water), shock waves, and ultraviolet light forming free, highly reactive radicals were reported to be responsible for the bactericidal effect. Additionally, the contamination of treated food due to chemical products from electrolysis, electrode erosion, and the disintegration of particulates within the food (by the shock waves) inhibited an industrial application of this process except for wastewater (Jeyamkondan et al. 1999).

The possibility of electrochemical reactions (electrolysis) occurring during PEF treatment has been first mentioned in 1960s by Sale and Hamilton (1967), who carried out a pioneering work on the use of PEF for microbial inactivation and showed the insignificance of electrolysis on the lethal effect of direct current (DC) pulses.

However, only since the 1980s electrochemical reaction in PEF treatment systems found increasing attention, when Dunn and Pearlman (1987) introduced an ion permeable polymer membrane functioning as a physical barrier between the electrodes and the liquid food in order to avoid electrode material from being released in the liquid food upon the application of PEF. However, this arrangement showed several drawbacks such as the possibility of using only monopolar pulses due to the selective nature of membranes, additional cost of membrane material and high sensitivity to puncture by any electrical discharges, frequently required maintenance, and complicated arrangement for industrial implementation. Due to these complexities, it was understood that the reduction of electrode reactions, rather than a complete prevention, might be preferred as long as the metal concentration remains within the limits dictated by food regulations.

In this line, Bushnell et al. (1995a, b) patented a method to avoid or reduce electrochemical reactions and the fouling of electrodes in a PEF processing system. Based only on a theoretical analysis, the authors suggested that the rate of electrophoresis and electrochemical reactions is proportional to the net electric charge delivered to the PEF chamber, and therefore, a claim has been made that a "zero-net-charge delivery" substantially prevents fouling of electrode(s) and reduces electrochemical reactions in general. Authors explained that, by removing all the residual charge at the electrode interface during the time elapsing between two consecutive pulses (zero-net-charge concept), no cumulative buildup of charges occurs and, hence, no electrochemical reactions will take place for any pulse of a width shorter than a certain threshold.

Few years later, a broad discussion of fundamental electrochemistry related to PEF has been given by Morren et al. (2003), who developed electrical equivalent circuit models to describe the behavior of the electrode/electrolyte interface under various conditions. Moreover, the authors performed the first attempt to study the release of electrode material into liquid product undergoing a PEF treatment. They exposed stainless steel electrodes in contact with an aqueous solution of NaCl to sinusoidal waveforms of only 15 and 150 V peak-to-peak voltages, resulting in a maximum electric field of 0.15 kV/cm and a maximum current of 480 mA, which were far below the typical PEF treatment conditions. This notwithstanding, the results have a certain relevance showing that at each voltage level the amount of the different elements (iron, chromium, nickel, and manganese) released from stainless steel electrodes is proportional to the width of applied pulses after a critical width.

Since then several researchers have addressed the problem of electrochemical reactions in PEF treatment systems highlighting that it is a very complex phenomena, which is largely unavoidable in the long-term trials, especially when PEF is carried out under severe treatment conditions (Pataro et al. 2014a). Most of the attention has been focused on the phenomenon of metal release and electrode corrosion and its dependence on the main operating parameters (Gad and Jayaram 2011, 2012a, 2014; Góngora-Nieto et al. 2002; Kim and Zhang 2011; Kotnik et al. 2001; Master et al. 2007; Morren et al. 2003; Pataro et al. 2014a, 2015a, b; Roodenburg et al. 2005a, b, 2010; Saulis et al. 2007). To this regard, numerical simulation has been recently applied as a valuable tool to improve the understanding of fundamentals of the electrochemical phenomena occurring at the electrode-liquid interface of a PEF chamber, clarifying the effects of the main electrical parameters, chamber design characteristics, and treatment medium composition on electrode corrosion or release of electrode's materials (Pataro et al. 2015a, b, 2017a, b).

Very little attention has been, instead, paid to possibility that reaction products (e.g., metal ions) and food constituents can participate in secondary chemical reactions also after pulse treatment has been completed, thus negatively affecting chemical and sensorial properties of food treated products and arising possible toxicity problems (Evrendilek et al. 2004; Rodaitė-Riševičienė et al. 2014; Sun et al. 2011; Zhao et al. 2012).

Therefore, additional work is needed to obtain more detailed insights on the influence on these phenomena on the technical feasibility of PEF technology as well as on safety and quality aspects of food products.

Electrochemical Behavior of a PEF Treatment Chamber

Ionic Double Layer and Electrode Reactions

In a PEF system the two metal electrodes of the treatment chamber are electrically connected by a high voltage cable to a pulse generator and placed in direct contact with a liquid food (or any electrolyte solution). From an electrochemical point of view, this system acts as an electrolytic cell where an external source of electrical energy is responsible for driving an electrical current through the cell. The current flowing in the conductive solid electrodes consists of free electrons, while in the conductive electrolyte solution, the current is carried by ions rather than by free electrons (Roodenburg et al. 2005a).

To understand the electrochemical behavior of a PEF chamber, it is necessary to identify the characteristics of the electrode/electrolyte interface.

Initially the PEF chamber can be considered as made with equal electrodes in contact with an electrolyte with homogeneous concentration. Before starting the pulse treatment (i.e., without externally applied voltage), immediately at each electrode-electrolyte interface, in order to maintain the condition of electroneutrality, a so-called double layer will develop. This layer, which consists of charged particles and/or of orientated dipoles (Fig. 1), behaves as an electrical capacitor (Morren et al. 2003). The formation of the double layer causes a potential drop ($\Delta\phi_{\mathrm{dl}}$) across the electrode-electrolyte interface, which tends asymptotically to zero at the imaginary boundary of the double layer. When no external voltage is applied across the electrodes, this potential drop is of the order of magnitude of mV and only low-level reactions occur at each electrode-electrolyte interface. In these conditions the two competing reactions reach an equilibrium, whereby the currents are equal with opposite sign leading to a zero net current flow (Morren et al. 2003).

During pulse treatment, due to the application of a potential difference across the electrodes, an electrical current pass through the cell occurs, and charges buildup across the double layer takes place (Bockris et al. 2002; Gileadi 1993a). In this case,

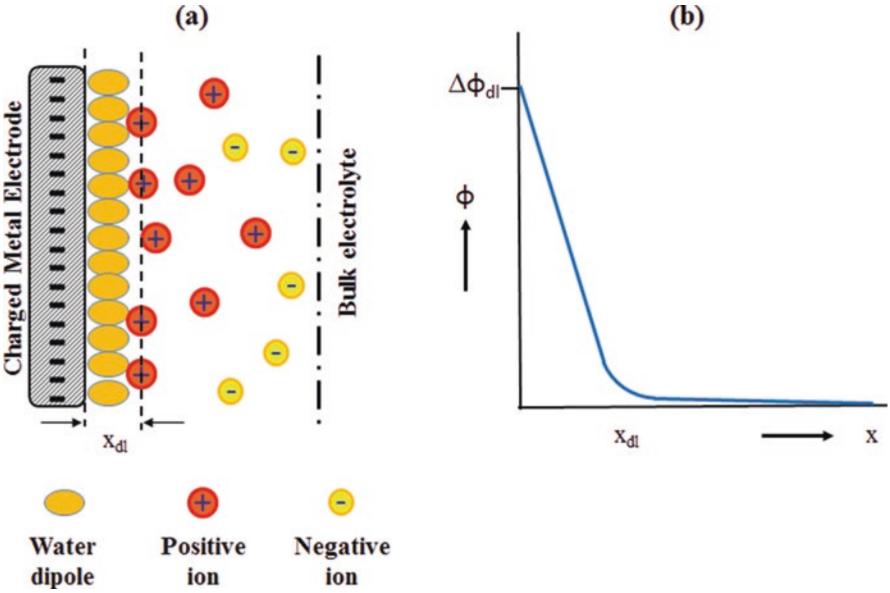


Fig. 1 (**a**) Schematic diagram of an ionic double layer at the electrode-electrolyte interface (x_{dl} is the thickness of the double layer); (**b**) variation of the electrostatic potential ϕ with distance x from the electrode surface

the charge density and the thickness (x_{dl}) of the ionic layers at the interface increase leading to an increase of the potential drop $\Delta\phi_{\mathrm{dl}}$.

As long as the potential across the double layer remains below the typical threshold voltage (U_{th}) of the reaction potential of reacting species (~1–2 V), no electrochemical reactions occur, except some low-level reactions due to the exchange current. The threshold voltage, or standard reduction potentials (E°_{red}), may be different for each of the electrode and depends, among others, on temperature, electrode material, pH, and the chemical content of the fluid (Pataro et al. 2017a, b).

If a high enough voltage is applied across the electrodes for a long enough time to let the voltage across the double-layer capacitor exceed the threshold value, in order to preserve the charge conservation principle, two independent electrochemical (Faradaic) half-cell reactions will occur at the electrode interfaces (Eqs. 1 and 2): oxidation half-cell reactions (i.e., loss of electrons) will take place at the electrode surface behaving as anode (i.e., high voltage electrode), and reduction reactions (i.e. gain of electrons) at the electrode surface behaving as cathode (i.e., grounded electrode) (Morren et al. 2003). As a result, the overall reactions (Eq. 3) produce periodic concentration changes of redox species at the electrode-electrolyte interfaces.

Anodic half-reaction:

$$R_{\mathrm{ed},2} \rightarrow \mathrm{O}_{x,2} + n \cdot e^{-} \tag{1}$$

Cathodic half-reaction:

$$\mathrm{O}_{x,1} + n \cdot e^{-} \rightarrow R_{\mathrm{ed},1} \tag{2}$$

Overall redox reaction:

$$\mathrm{O}_{x,1} + R_{\mathrm{ed},2} \rightarrow R_{\mathrm{ed},1} + \mathrm{O}_{x,2} \tag{3}$$

where $\mathrm{O}_{x,1}$ and $R_{\mathrm{ed},1}$ are, respectively, the oxidized and reduced form of the chemical species 1; $\mathrm{O}_{x,2}$ and $R_{\mathrm{ed},2}$ are, respectively, the oxidized and reduced form of the species 2; and n is the number of electrons (e^{-}) exchanged during the reaction.

If during PEF treatment monopolar pulses are applied, the electrode connected to high voltage will behave as anode, while the grounded electrode will behaves as cathode. If instead bipolar pulses are applied, the cathode and anode interchange places according to the pulse repetition frequency and, therefore, oxidative and reductive half-reactions will occur alternatively at the same electrode site (Roodenburg et al. 2005a; Pataro et al. 2017a, b).

The electrode reactions involve mass transport of electro-active species to the electrode, electron transfer across the electrode interface, and the mass transport of the reaction products back to the solution. Mass transport and charge transfer are two consecutive processes whose rate depends, besides the applied potential, on electrode material, electrolyte, pulse repetition frequency, pulse polarity, temperature, and pH, among others. The slower the two processes is, therefore, the limiting step determines the overall rate (Gileadi 1993b; Morren et al. 2003; Pataro et al. 2015a).

During PEF treatment, and especially when high treatment intensities are applied, a variety of electrochemical reactions may simultaneously occur at the electrode-food interfaces involving chemical species of either electrode material or food product (Pataro et al. 2020). Since predicting all possible electrochemical reactions during the PEF processing of any real liquid food is a very complex task, for simplicity, only few examples of potential anodic and cathodic half-cell reactions related to electrolysis of water and corrosion will be presented in the following equations (Gad and Jayaram 2014).

Cathodic half-reactions:

$$\mathrm{Cl}_{2(\mathrm{gas})} + 2e^- \Rightarrow 2\mathrm{Cl}^-_{(\mathrm{aq})} \tag{4}$$

$$\mathrm{O}_{2(g)} + 4\mathrm{H}^+_{(\mathrm{aq})} + 4e^- \Rightarrow 2\mathrm{H}_2\mathrm{O}_{(\mathrm{liq})} \tag{5}$$

$$\mathrm{O}_{2(g)} + 2\mathrm{H}^+_{(\mathrm{aq})} + 2e^- \Rightarrow 2\mathrm{H}_2\mathrm{O}_{2(\mathrm{liq})} \tag{6}$$

$$2\mathrm{H}^+_{(\mathrm{aq})} + 2e^- \Rightarrow \mathrm{H}_{2(\mathrm{gas})} \tag{7}$$

$$2\mathrm{H}_2\mathrm{O}_{(\mathrm{liq})} + 2e^- \Rightarrow \mathrm{H}_{2(\mathrm{gas})} + 2\mathrm{OH}^-_{(\mathrm{aq})} \tag{8}$$

Anodic half-reaction:

$$2\mathrm{H}_2\mathrm{O}_{(\mathrm{liq})} \Rightarrow \mathrm{O}_{2(g)} + 4\mathrm{H}^+_{(\mathrm{aq})} + 4e^- \tag{9}$$

$$2\mathrm{H}_2\mathrm{O}_{(\mathrm{liq})} \Rightarrow 2\mathrm{H}_2\mathrm{O}_{2(\mathrm{liq})} + 2\mathrm{H}^+_{(\mathrm{aq})} + 2e^- \tag{10}$$

$$v_1\mathrm{M}_{(s)} + v_2\mathrm{H}_2\mathrm{O}_{(\mathrm{liq})} \Rightarrow \mathrm{M}_{v1}\mathrm{O}_{v2} + 2v_2\mathrm{H}^+_{(\mathrm{aq})} + 2v_2e^- \tag{11}$$

$$\mathrm{M}_{(s)} \Rightarrow \mathrm{M}^{n+}_{(\mathrm{aq})} + n\,e^- \left(\mathrm{M} = \mathrm{Fe,Ni,Cr,Mn,Ti,Pt,}\ldots\right) \tag{12}$$

Which of the half-reactions occurs depends on the relative ease of each of the competing reactions.

After pulsing (i.e., when PEF system is switched off), due to either concentration differences around the electrodes or to surface material changes, the behavior of cell may shift from electrolytic to galvanic. Thus, if the treatment chamber is not dried up, some of the products of those electrochemical reactions may spontaneously initiate a number of secondary chemical reactions, which may involve food components, even with no external voltage applied (Pataro et al. 2020).

Electrical Equivalent Circuit

The relationship between an external electrical perturbation at the terminals of a PEF chamber and the response of the double layer at each electrode interface can be described by an equivalent electrical circuit. In Fig. 2, simplified equivalent electrical circuits for the PEF treatment chamber with electrode-electrolyte interfaces are

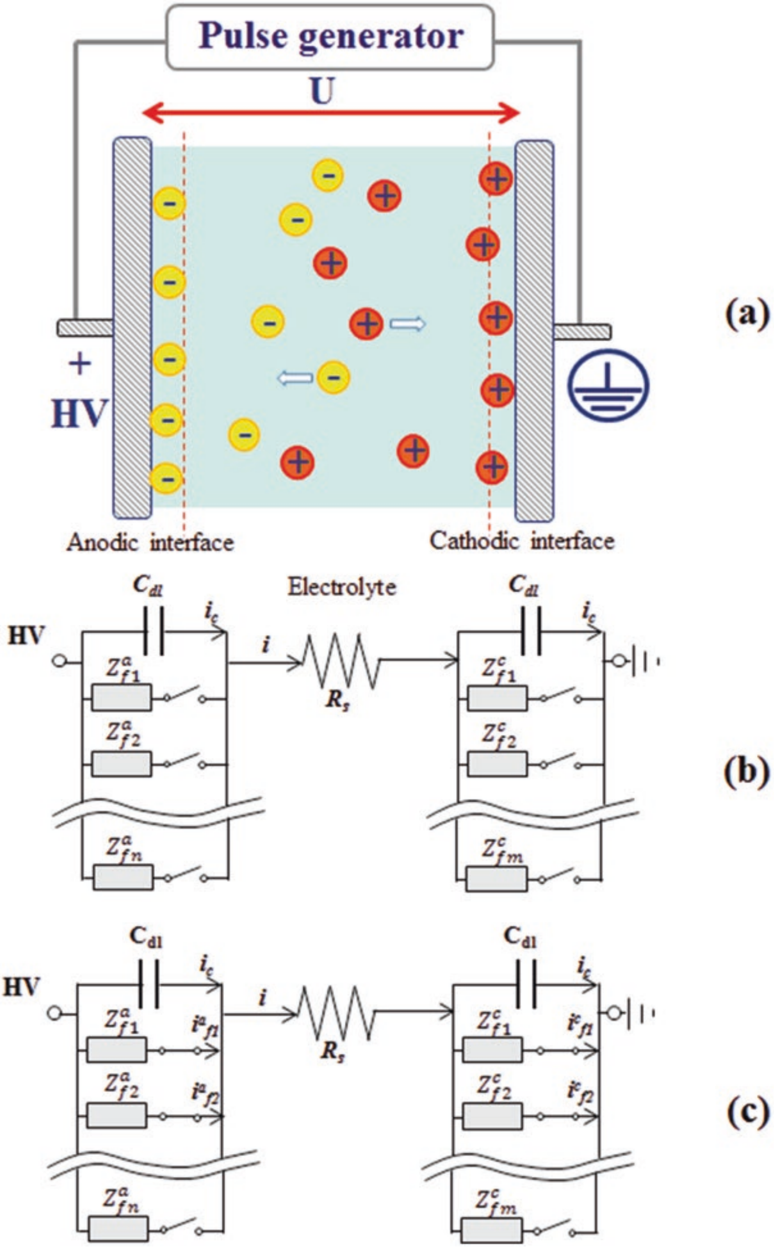


Fig. 2 Electrical equivalent circuit for the PEF treatment chamber with electrode-electrolyte interfaces. (**a**) schematic of a parallel plate PEF chamber with a pulse generator; (**b**) equivalent circuit with no Faradaic reactions; (**c**) equivalent circuit with Faradaic reactions. C_{dl} is the double-layer capacitance; R_s is the bulk resistance of the electrolyte solution; Z^a_{fk} is the anodic Faradaic impedance in the branch k (k = 1…n); Z^c_{fp} is the cathodic faradaic impedance in the branch p (p = 1…m); i^a_{fk} and i^c_{fp} represent the anodic and cathodic Faradaic current passing in the branch k and p, respectively

shown for different conditions. An external dc source of voltage (U) is applied to a conductive electrolyte through the metal electrodes of the PEF chamber. In the equivalent circuits, R_s represents the bulk resistance of the solution, while the ohmic resistance of both electrodes is negligible. Each electrode-electrolyte interface is analogous to a parallel combination of the double-layer capacitance C_{dl}, which is involved in the charging process of the double-layer capacitor by a non-Faradaic current, and a number of branches (n at anode and p at cathode), each consisting of a normally open switch in series with a Faradaic impedance Z_f (Z^a_{fk} at the anode and Z^c_{fp} at the cathode). The Faradaic impedances, which are used to model the Faradaic process associated to each of the possible half-cell reactions that might occur at the anodic and cathodic interface (Gad and Jayaram 2014), include resistors for the Faradaic processes and electrolyte transport, and Warburg impedance for diffusional limitations whenever applicable (Bockris et al. 2002; Gileadi 1993b, c; Morren et al. 2003; Pataro et al. 2015a). The switches are controlled through the corresponding double-layer potential ($\Delta\phi_{\mathrm{dl},a}$ at the anode and $\Delta\phi_{\mathrm{dl},c}$ at the cathode), i.e., each switch will close when the capacitor potential exceeds the threshold voltage ($U_{\mathrm{th},i}$) characteristic of a given electrode reaction i (Gad and Jayaram 2014).

These models do not take into account some peculiar factors such as the heterogeneity of electrode surface and the eventual formation of reaction intermediates absorbed at the electrode surface. Moreover, the circuit is nonlinear being C_{dl} and Z_f dependent on potential (Gileadi 1993b).

Initially, when an external voltage (U) is applied, and the threshold voltage at which the half-cell reactions ($U_{th,i}$) typically start is not reached yet, the model takes the form of Fig. 14.2b. In this phase, the current (i) starts flowing through the electrolyte resistance, and only a capacitive, non-Faradaic charging current (i_c) is flowing in C_{dl}. This current is called charging current (i_c) since it is responsible for charging the double-layer capacitor up to the reaction potential (U_{th}) of the reacting species (Morren et al. 2003). The time required for this charging process is called threshold time (t_{th}, in μs) and is given by the following equation (Morren et al. 2003):

$$t_{\mathrm{th}} = \frac{C'_{\mathrm{dl}} U'_{\mathrm{dl}}}{j} \tag{13}$$

where j is the current density (in A cm^{-2}) through the chamber, while the quoted parameters represent the equivalent values of the specific capacitance (capacitance per unit of area, C_{dl}, in μF cm^{-2}) and reaction potential (U_{th}, in V) of the two electrode-electrolyte interfaces in series (i.e., $C'_{\mathrm{dl}} = (1/2)\bullet C_{\mathrm{dl}}$ and $U'_{\mathrm{th}} = 2\bullet U_{\mathrm{th}}$). From Eq. 13, it can be seen that, for a given electrode reaction, the threshold time depends mainly on the current density, which in turn depends on the applied voltage, fluid conductivity, and chamber geometry, as well as on the value of the double-layer capacitance.

As soon as the potential of one capacitor ($\Delta\phi_{\mathrm{dl},a}$ *or* $\Delta\phi_{\mathrm{dl},c}$) exceeds the reaction potentials ($U_{\mathrm{th},i}$) of one or some of the possible anodic or cathodic half-cell reactions, the switches in the corresponding branches close, and the currents ($i_{\mathrm{f,i}}$) start flowing through the impedance element ($Z_{\mathrm{f,i}}$), and the circuit appearing in Fig. 2c holds. The current flowing through either Z_{fk}^{a} or Z_{fp}^{c} elements is a Faradaic current since it is involved in electrochemical half-cell reactions and represents a direct measure of the rate of the reactions taking place at the electrode-electrolyte interfaces. Dividing of the total current (i) passing through the treatment chamber among the half-cell reactions depends on their reaction potential and relative rates. Faraday's law governs the relationship between the amount m_{rs} (in g) of a species s produced by the reaction r, and the cumulative electrical charge Q_r (in C) transferred by the reaction over a period of time, i.e.,

$$m_{\mathrm{rs}} = \frac{Q_r}{F}\frac{M_s}{n_{\mathrm{rs}}} \tag{14}$$

where $F = 96{,}485\ \mathrm{C\ mol^{-1}}$ is the Faraday constant, M_s is the molar mass of the substance s (in g mol^{-1}), and n_{rs} is the number of electrons transferred for each product s formed by reaction r. The ratio M_s/n_{rs} is the equivalent weight of the species s.

From the preceding discussion, the occurrence of electrode reactions might be avoided or minimized by maintaining the capacitor potential below the reaction potential of the reacting species through controlling the shape (amplitude/width) and protocol of the applied pulses, a proper design of circuit topology and treatment chamber, and the chemical-physical properties of the food product undergoing PEF process.

Factors Affecting Electrode Reactions

The extent of the electrochemical reactions occurring at the electrode-electrolyte interface of a PEF chamber is mainly related to the total amount of electrical charge passing through the electrode-electrolyte interface during the pulse treatment, which is in agreement with the Faraday's law.

The total charge transferred per each pulse Q_p (in C) depends primarily on current i (in A) and pulse duration τ (in s), where the current depends indirectly on food conductivity (σ), applied voltage (U), and chamber geometry. The transferred charge can be calculated by integrating the current density vector $\boldsymbol{j}$ at the interface area (Eq. 15). For conductive media the current density vector $\boldsymbol{j}$ equals $\sigma \cdot \boldsymbol{E}$ (Roodenburg et al. 2005a).

$$Q_p = \int_0^{\tau} |i|\,\mathrm{d}t = \iint_0^{\tau} \int_{A_i} |\boldsymbol{j}|\,\mathrm{d}\boldsymbol{A}\,\mathrm{d}t = \iint_0^{\tau} \int_{A_i} |\sigma \cdot \boldsymbol{E}|\,\mathrm{d}\boldsymbol{A}\,\mathrm{d}t \tag{15}$$

where $\boldsymbol{j}$ is the local time dependent current density (in A m^{-2}), $\boldsymbol{A}$ is the oriented surface of the interface (in m^2), σ is the electrical conductivity of the treated medium (in S m^{-1}), and $\boldsymbol{E}$ is the electric field vector (in V m^{-1}).

The total transferred charge (Q_{tot}, in C) during a PEF treatment can be determined by multiplying the charge delivered per pulse (Q_p, in C/pulse) by the total number of pulses (n_p) (Eq. 16). The number of pulses (n_p) is generally set for a batch treatment chamber, while for a continuous flow treatment chamber, it can be evaluated by multiplying the pulse repetition frequency (f, in Hz) and the residence time (t_r, in s) of the product in the chamber, which in turn can be estimated as the ratio of the treatment volume (v, L) and the volumetric flow rate (F_v, L s^{-1}).

$$Q_{\text{tot}} = n_p \cdot Q_p = f \cdot t_r \cdot Q_p = f \cdot \frac{v}{F_v} \cdot Q_p \tag{16}$$

It should be also noted that the total charge passing through the PEF chamber is strictly related to the total specific energy input W_T, which, along the field strength E, is one the main process parameters that define the PEF treatment intensity (Eq. 17):

$$W_T = n \cdot W_p = n \cdot \frac{Q_p \cdot U}{v} = \frac{f \cdot Q_p \cdot U}{F_v} = \frac{Q_{\text{tot}} \cdot U}{v} \tag{17}$$

where W_p is the specific energy input per pulse (in J L^{-1} pulse^{-1}).

However, besides the total amount of charge transferred, the way of delivering the electrical charge also affects the rate of charging and discharging of the double-layer capacitors, thus affecting the rate and the amount of electrochemical reactions.

From Eqs. (13, 15, and 16), it can be inferred that the extent and the rate of the electrochemical reactions occurring at the electrode-electrolyte interface of a PEF chamber depend on many factors, which are related to each other and that can be classified into three groups: processing parameters, design parameters, and treatment medium characteristics. An adequate knowledge of the influence of these factors and their interactions on the extent of the electrochemical reactions occurring at the electrode-electrolyte interface is necessary to establish optimal PEF treatment conditions, circuit topology of the pulse generator, geometry and material of electrodes, and food characteristics allowing to minimize any undesired side effect related to these reactions.

Processing Parameters

As it can be inferred from the Eqs. (13 and 15, 16, 17), for a given chamber geometry and treatment medium characteristics, the main PEF processing parameters that can affect the buildup of charge on the double-layer capacitors and, consequently, the extent and rate of electrode reactions are electric field strength, energy input, pulse width, and pulse polarity.

In general, at a fixed pulse width, increasing the field strength (i.e., applied voltage) and energy input (i.e., number of pulses or treatment frequency) will increase the total transferred charge through the electrode-electrolyte interface (Eqs. 15, 16 and 17), as well as the charging rate (Eq. 13) of the double-layer by increasing the current density. However, it was shown that variation in the applied voltage, within the typical PEF conditions for microbial inactivation, did not have a remarkable effect on the extent of electrochemical reactions (Gad and Jayaram 2014). On the other hand, instead, the pulse repetition frequency, which is the main processing parameter that need to be adjusted when operating in a continuous flow mode to deliver the desired amount of energy through the treatment chamber, plays a crucial role on the charging rate of the double-layer capacitors, especially when monopolar pulses are applied (Pataro et al. 2014a, 2015b). In particular, as the pulse frequency increases upon increasing the energy input (Eq. 17), the time interval between two consecutive monopolar pulses decreases resulting in only a partial discharge of the double-layer capacitor at each electrode-electrolyte interface, before the next pulse will be applied. As a consequence, charges will be accumulated on the double layer at a faster rate as the frequency increases, and when the threshold voltage is exceeded, electrochemical reactions will occur causing the corrosion of the electrodes or other undesired side effects (Pataro et al. 2014a, 2015b). This explanation agrees with the concept of charging the double-layer capacitors as well as with the need to avoid a cumulative buildup of charge discussed in Morren et al. (2003).

In addition to field strength, energy input and frequency, electrochemical reactions are also dependent on pulse width and pulse polarity since these parameters may affect the charging rate of the double-layer capacitance.

It has been shown that, when the applied voltage is kept the same, shorter pulses lead to a lower amount of electrochemical reaction (Gad and Jayaram 2014; Morren et al. 2003). To explain the effect of pulse width, Gad (2014) suggested that, from the perspective of each half-cell reaction, the width of each pulse can be divided into two parts. In the first part, the double layer is charged as long as its potential remains below the potential reaction of the reacting species. For a given electrode material (i.e., for a given double-layer capacitance), the duration of the first part depends on the current (i.e., applied voltage) and remains unchanged (Eq. 13). The second part starts when the potential reaction is reached and thus the half-cell reaction occurs. With shorter pulses, the second part of the pulse (when electrode reactions occur) is shortened considerably. This is in agreement with Eq. (13) that gives a trade-off between current density and pulse duration for a certain treatment chamber geometry. A higher field strength in the same treatment chamber (i.e., a higher applied voltage) results in a higher current density. Thus for higher field strength, the pulse duration should be decreased. Therefore, the optimum pulse should feature relatively short pulse width with an applied voltage satisfying the minimum field strength required for microbial inactivation (Gad and Jayaram 2014).

As compared to monopolar pulses, bipolar or oscillatory pulses featuring a ratio between positive and negative pulses closer to unity may prevent electrochemical reactions by the same concept of zero-net-charge delivery (Bushnell et al. 1995b; Roodenburg et al. 2005a), where both double-layer capacitors are partially but continuously charged and discharged without reaching the threshold potential (U_{th}) corresponding to the onset of anodic and cathodic Faradaic reactions (Amatore et al. 1998). Under such circumstances, the current flowing through the cell would be purely capacitive leading to only a formal displacement of charges from one double layer to the double layer of the other electrode (Gad 2014).

Design Parameters

The extent of electrophoretic phenomena and electrochemical reactions at the electrode-electrolyte interface of a PEF chamber is also affected by circuit topology of the pulse generator, treatment chamber geometry, and electrode materials.

Besides the generation of a given pulse shape, a proper design of the circuit topology can enable to force double-layer discharging based on the concept of “zero-net-charge delivery,” which substantially reduces the extent of electrophoretic and electrochemical effects (Bushnell et al. 1995a, b). In this line, Gad and Jayaram (2014) designed a pulse generator characterized by a bidirectional nature of the current waveform, which was used to ensure zero-net-charge delivery with monopolar pulses. Based on this principle, the charging current of the generator’s capacitor was allowed to pass through the PEF processing chamber in one direction, and then, the pulse current generated during the capacitor discharging phase flowed in the opposite direction. Thus, the current flowing through the chamber during the capacitor-discharging phase removes any charge remaining on the double layer from the capacitor-charge phase. Thus, the accumulation of charge on the double layer from one pulse to another can be avoided.

From Eq. (13), it can be inferred that, for a given electrode reaction and external applied voltage, the threshold time depends mainly on the current (density) through the electrical resistance of the PEF chamber and the value of the double-layer capacitance of the electrode material.

Thus, PEF treatment chamber geometries featuring high intrinsic electrical resistance, which, therefore, operate at a relatively low current, may limit the occurrence of electrochemical reactions (Gongora Nieto et al. 2002). Different types of electrode arrangement have been proposed both for static and continuous chamber, with the most commonly used having been parallel plate and co-field configuration. Parallel plate electrodes configuration are the simplest in design and produce the most uniform distribution of the electric field. They are typically characterized by a large electrode surface and low intrinsic electrical resistance (from few ohms to tens of ohms) (Gongora-Nieto et al. 2002; Raso et al. 2016). Therefore, this configuration generally operates at relatively high current density, which makes shorter the charging time of the double-layer capacitance. On the other hand, a co-field chamber configuration cannot develop a constant electric field across the gap (as with parallel plate), thus yielding nonuniform treatment. However, such configuration has advantageous fluid dynamics, highly desiderate for food processing and convenient for cleaning in place, as well as a high intrinsic electrical resistance (of the order of hundreds of ohms) due to the low effective area in the cross section of the tubular electrodes (Gongora-Nieto et al. 2002). Thus, this configuration typically operates at lower current density than the parallel plate configuration, which makes it suitable for limiting the occurrence of electrode reactions (Eq. 13).

Similarly, the use of high capacitance electrode materials, such as platinum ($C_{dl} = 48\ \mu F/cm^2$), titanium ($C_{dl} = 50\ \mu F/cm^2$), glassy carbon ($C_{dl} = 260\ \mu F/cm^2$), or dimensionally stable anode (DSA) ($C_{dl} = 2000\ \mu F/cm^2$), instead of the most commonly used stainless steel electrodes ($C_{dl} = 35\ \mu F/cm^2$), may limit the occurrence of electrode reactions. In fact, according to Eq. (13), the use of electrode material with high C_{dl} values may slow down the charging process of the double-layer capacitor, avoiding its full charging before the next pulses is applied (Amatore et al. 1998; Góngora-Nieto et al. 2002; Pataro and Ferrari 2020). Moreover, on the basis of the same principle of avoiding full charging of the double-layer capacitors, it has been found that the extent of the electrochemical reactions may be limited by using electrode materials featuring higher resistance to electrochemical reactions such as titanium and platinized titanium (Amatore et al. 1998; Gad et al. 2014; Kim and Zhang 2011).

Treatment Medium Characteristics

The composition as well as chemical physical properties of the treatment medium can significantly affect the type and the extent of the electrophoretic phenomena and electrochemical reactions occurring at electrode-electrolyte interface.

In rich-protein foods such as milk, a film of material can collect or agglomerate on at least one electrode via electrophoretic process leading to the so-called fouling of the electrodes.

On the other hand, many food products contain halides such as chlorides, which are aggressive anions which may damage the thin oxide layer on the passivated metal electrode surface protecting the metals against corrosion. Thus the presence of these active species may contribute to the enhancement of the oxidation half-cell reactions at the anode, including those causing the release of metals from the electrodes (Pataro et al. 2014a, 2015b).

Also electrical conductivity and pH of the treatment medium may affect the extent of electrode reactions. Acidic food products, such as most fruit juices, may face higher problems with electrode material migration than nonacidic products, especially when PEF is carried out under severe processing conditions using electrochemically active electrode material (e.g., stainless steel) (Amatore et al. 1998; Gad and Jayaram 2011, 2012a; Pataro et al. 2012, 2014a, b; Roodenburg et al. 2005b). This can be explained by knowing that lower pH means higher concentration of hydrogen ions at the cathode. As a result, the cathodic half-reaction (Eq. 18) could couple with the anodic half-reaction (Eq. 19) resulting in accelerated corrosion and hydrogen generation (Eq. 20) compared to those at the neutral pH value (Amatore et al., 1998).

Cathodic half-reaction:

$$2\mathrm{H}^{+}_{(\mathrm{aq})} + 2e^{-} \leftrightarrow \mathrm{H}_{2(g)} \tag{18}$$

Anodic half-reaction:

$$\mathrm{M}_{(s)} \leftrightarrow \mathrm{M}^{2+}_{(\mathrm{aq})} + 2e^{-} \tag{19}$$

Overall reaction:

$$\mathrm{M}_{(s)} + 2\mathrm{H}^{2+}_{(\mathrm{aq})} \leftrightarrow \mathrm{M}^{2+}_{(\mathrm{aq})} + \mathrm{H}_{2(g)} \tag{20}$$

where M = Fe, Cr, Ni or any other metallic components of the electrode material.

Thus, for treating of acidic products, including beverages such as orange juice, the use of more inert materials may be an interesting way for markedly reducing the extent of electrode corrosion and electrochemical phenomena that occur at the electrode-solution interface (Gad and Jayaram 2012b). The effect of the type of acid, however, requires further investigation.

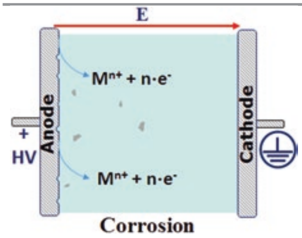
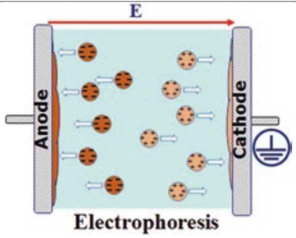
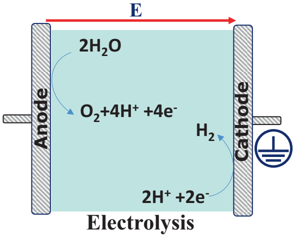
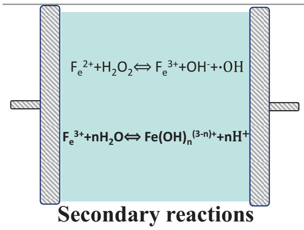
On the other hand, highly conductive foods such as tomato juice, milk, and orange juice may experience a higher rate of electrode material migration (Amatore et al. 1998; Gad and Jayaram 2012b; Pataro et al. 2012), due to the high current flow passing through the medium with high conductivity, which lead to a higher charging rate of the double-layer capacitors (Eq. 13). As a result, according to Eq. (13), beverages such as orange juice, which has a typical conductivity of 0.3 S/m, can be treated with a longer pulse than tomato juice, which has a typical conductivity of 2 S/m.

Side Effects of Electrochemical Phenomena and Challenges

During PEF treatment electrophoresis-based phenomena (electrode fouling) as well as various electrochemical reactions can potentially occur, including those involving chemical changes in food products, electrode corrosion, and electrolysis of water. In addition, some of the products of those electrochemical reactions may initiate a number of secondary chemical reactions involving food components, even after pulse treatment has been completed. These reactions are unavoidable, especially for those applications requiring high treatment intensity (e.g., microbial inactivation) and lead to undesired effects, which may hamper commercialization of the PEF process through technological, safety, quality, and costs aspects (Pataro and Ferrari, 2020), as depicted in Table 1.

Electrode corrosion is one of the main consequences of the electrochemical reactions occurring at the electrode-electrolyte interface of a PEF treatment chamber. The dissolution of the anode material due to oxidation of the metal of the electrode

Table 1 Side effects of electrochemical phenomena occurring in the operation of a PEF treatment chamber (Pataro and Ferrari, 2020)

Electrophoresis, electrochemical phenomena, secondary reactions	Process and technological issues	Effects on Food safety and quality
	Distortion or local enhancements of the electric field Electric arcs formation Short electrode lifetime Reduced reliability and life time of pulse generator	Health safety regulation Alteration in color, flavor, and taste (metallic mouth feeling) Toxic compounds Formation of high reactive species (free radicals) Food disintegration (by-products)
	Electrode fouling Electric arcs formation Short electrode lifetime Reduced reliability and life time of pulse generators Interruption of the flow of the product	Contamination of the processed food Formation of high reactive species (free radicals)
	Gas bubble generation Electrode corrosion Electric arcs formation Reduced reliability of and lifetime of pulse generators	Oxidative degradation of food components Formation of toxic compounds (H_2O_2) Under-processing of food
	Contamination of the system (rust formation)	Local changes of pH Generation of reactive oxygen species (ROS) Oxidative degradation of food constituents Production of active chlorine species (ACS) Toxicity problems

M^{n+} migrated metal ions, ⁂ piece of anode material (pitting corrosion), ⊖ negative-charged particles, ⊕ positive charged particles

(Eq. 12) along with detachment of small particles of electrode material (pitting corrosion) is responsible for this phenomenon.

The electrode material released into the PEF processed foods are basically contaminants and may have some toxic potential, as well as affect food quality, equipment reliability, treatment efficiency, and electrode lifetime (Evrendilek et al. 2004; Morren et al. 2003; Pataro et al. 2014a, b, 2015b; Roodenburg et al. 2005a,b; Saulis et al. 2007).

For the safety aspect of PEF processing, the type and amount of electrode material released in the processed products must be within the health safety regulations before introducing it as processed food to the market (Gad and Jayaram 2012a; Roodenburg et al. 2005a). By reviewing the regulations for food industries dictated by governments in Europe and USA (CODEX STAN 193–1995; CODEX STAN 247–2005; USDA 2018), they have been mainly concerned with the presence of heavy/toxic metals, namely, cadmium, lead, and mercury, while no standards are given for the maximum concentration of dissolved metallic elements typically constituting the materials used as electrodes in a PEF chamber. Only for some of them, such as the main metallic elements of stainless steel, which is one of the most popular electrode materials of PEF chamber, guidelines could be taken from drinking water regulations (Directive No 98/83/EG; U.S. EPA 2009), as shown in Table 2.

Apart from safety aspects, the release of electrode material in the product may cause alteration in color, flavor, and taste (metallic mouth feeling) of PEF processed foods, which may stand against consumers' acceptance to this technology (Evrendilek et al. 2004; Gad and Jayaram 2012b; Sun et al. 2011). Thus, sensory analyses should be performed to evaluate the acceptance of PEF processed products against either conventionally or unconventionally processed foods or fresh products.

Finally, corrosion can cause serious damages to the electrodes, whose surface roughness can markedly increase as a consequence of the metal release from the anode and, in part, as partial deposition of metal oxides on the cathode (Kim and Zhang 2011; Pataro et al. 2014a; Roodenburg et al. 2005a; Saulis et al. 2007). This might create distortion or local enhancements of the electric field, which may markedly impair PEF treatment uniformity as well as reduce treatment efficiency during the operation (Donsì et al. 2007; Jaeger et al. 2009; Pataro et al. 2011, 2014a, b; Saulis et al. 2007). Moreover, the increase in surface roughness may trigger arcs formation (dielectrical breakdown of food) within the treatment chamber, which may likely promote the formation of high reactive species (e.g., free radicals), as well as reduce the reliability of pulse generator (e.g., switching devices) and the lifetime of electrodes (pitting corrosion) to few hours of operation (Kim and Zhang 2011; Gad et al. 2014; Saulis et al. 2007; Pataro et al. 2014a; Roodenburg et al. 2005b; Toepfl et al. 2007), thus reducing the technical feasibility of PEF technology.

Fouling of the electrodes is another undesirable side effect that is believed to be due to electrophoresis accompanying the flow of electric current during PEF processing. Specifically, under the influence of the external electric field, charged particles (e.g., relatively large protein molecules or other fouling agent) suspended in the liquid food product are moved toward the oppositely charged electrode where they are collected, or agglomerated, to form a film of food particles (Bushnell et al. 1995a, b). The formation of such a film on the electrode(s) during extended processing periods can cause local electric field distortion, arcing, contamination of the system, and, in some cases, the interruption of the flow of the product (Bushnell et al. 1995a, b).

Electrolysis of water, which is largely contained in food subjected to PEF treatment, may also occur generating H_2 and O_2 gases (Eqs. 7, 8, and 9) at the electrode-solution interfaces. In addition, especially when there is a significant amount of

Table 2 Maximum contamination levels of metallic elements of stainless steel dictated by European legislation (Directive No 98/83/EG) and US regulations for drinking water

Concentration level of metallic elements (μg/L)				Regulation
Fe	Cr	Ni	Mn	
200	50	20	50	*Directive No 98/83/EG*
300[a]	100[b]	NA	50[a]	*U.S. EPA 2009*

[a] National Secondary Drinking Water Regulations are non-enforceable guidelines regarding contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water

[b] National Primary Drinking Water Regulations (NPDWRs) are enforceable standards that are established to protect the public against consumption of drinking water contaminants that present a risk to human health

chloride ions in the treated medium, cathodic half-reactions for electrolysis (Eqs. 7 and 8) may be also coupled with the anodic half-reaction (Eq. 4), resulting in $H_{2(g)}$ and $Cl_{2(g)}$ generation. The liberation of oxygen by electrolysis may further promote electrode corrosion (Tzedakis et al. 1999) as well as induce degradation of food components (e.g., phenolic compounds, lipids, and vitamins like ascorbic acid) and the formation of toxic compounds, such as H_2O_2 (Eq. 6) (Morren et al. 2003). Moreover, the presence of gas bubbles formed by electrolysis increases the chance of the occurrence of dielectric breakdown and arcing, thus causing technological and food safety problems and reducing the treatment efficiency (Góngora-Nieto et al. 2003; Toepfl et al. 2007).

Finally, products generate from electrochemical reactions during PEF treatments may initiate a number of secondary chemical reactions by reacting each other or involving food constituents, which may lead to changes in chemical composition, organoleptic attributes, and physical properties of processed food products, as well as the formation of toxic compounds even after the pulse treatment has been completed (Morren et al. 2003; Pataro and Ferrari 2020).

For example, secondary reactions triggered by corrosion and electrolysis products may induce local changes of pH in the vicinity of electrode surfaces, which may affect activity and stability of enzymes and microbial resistance to PEF treatments (Meneses et al. 2011; Rodaitė-Riševičienė et al. 2014). Moreover, the migrated metal ions along with pH changes can affect degradation of natural antioxidant compounds such as ascorbic acid (Assiry et al. 2006), as well as the stability of pigments such as anthocyanins (Sun et al. 2011), thus potentially altering color and nutritional and functional properties of food products. Corrosion and electrolysis products may also generate reactive oxygen species (ROS) such as hydroxyl (•OH), hydroperoxyl (•OOH), superoxide anion (O_2•−) radicals, H_2O_2, and singlet oxygen ($1O_2$), which may cause oxidative degradation of lipids, vitamins, and amino acids/proteins, thus potentially leading to production of undesirable flavor, toxic, and color compounds, which make foods less acceptable or unacceptable to consumers (Zhao et al. 2012).

In product containing chloride compounds, as many food products do, secondary reactions triggered by electrolysis products (e.g., Cl_2, Eq. 4) can result in the production of active chlorine species (ACS) with high redox potentials, such as hypochlorous acid (HOCl) and hypochlorite anions (OCl). The formation of these compounds can cause toxicity problems, even though they may also act as bactericides, thus improving the preservation efficiency of PEF treatment (Zhao et al. 2012).

Based on the above discussion, there is a challenge to assess whether the side effects are within the acceptable limits or to provide feasible strategies to eliminate, or at least reduce, the extent of electrochemical phenomena that cause these undesired effects. Specifically, although dissolution of electrode materials and other electrochemical reactions are largely unavoidable in the long term, their limitation is possible by either avoiding full charging of the double-layer capacitors, or using chemically inert electrode materials.

To this regard, for the PEF treatment of a given food product, strategies such as reduction of the buildup area (as in the case of co-field chambers) keep the applied voltage, pulse length, and frequency as the minimum value required for generating sufficient electric field and electrical energy for the specific application, as well as using bipolar pulses and electrode material having a high specific double-layer capacitance can help to significantly reduce the amount of electrochemical reactions (Amatore et al. 1998; Gad and Jayaram 2012a, 2014; Góngora-Nieto et al. 2002; Kotnik et al. 2001; Pataro et al. 2014a, 2015b; Roodenburg et al. 2005a, b). Similarly, proper design of pulse generator equipped with switching devices with a very low leakage current or by inserting a pulse transformer into the system may also reduce the amount of electrochemical reactions (Mastiwijk 2007). On the other hand, replacing commonly used stainless steel electrodes by more inert material such as titanium electrodes may be one solution to overcome this problem (Kim and Zhang 2011; Gad and Jayaram 2014; Toepfl et al. 2007). Also homogeneity of the electric field within the treatment zone, reduction and generation of enhanced field area, polishing of electrode surface after the mechanical machining (i.e. lathe), as well as degassing the food product before PEF treatment are other important design criteria and strategies for avoiding or limiting undesired electrochemical effects at the electrode-media interface (Pataro and Ferrari 2020).

Conclusions

Today, the first successful industrial applications of PEF processing in food industry have been achieved, especially as a pre-processing step to facilitate cutting operation in potato processing industry, where low or moderate PEF treatment intensities are required. In the food sector of fruit juice preservation, instead, where high treatment intensity along with and highly homogeneous treatment are required, several disadvantages and limitations still remain, such as those related with the electrophoretic and electrochemical phenomena occurring at the electrode-food interface of a PEF treatment chamber, which are unavoidable in long-term trials or when large amount of electrical charge is transferred through the electrodes.

The occurrence of electrochemical phenomena, especially those leading to corrosion and fouling of the electrodes, electrolysis of water, migration of electrode material components, and chemical changes, may seriously affect PEF commercialization through safety, quality, and technological and cost aspects.

The present challenge is to reduce the amount of electrochemical reactions by modifying the pulse generator systems, improving treatment design, and selecting more inert electrode materials and minimum treatment intensity, while taking into account chemical-physical properties of food under treatment, in order to improve the technical feasibility of PEF technology as well as to maintain chemical food safety.

References

Amatore C, Berthou M, Hebert S (1998) Fundamental principles of electrochemical ohmic heating of solutions. J Electroanal Chem 457:191–203

Arnal ÁJ, Royo P, Pataro G, Ferrari G, Ferreira VJ, López-Sabirón AM, Ferreira GA (2018) Implementation of PEF treatment at real-scale tomatoes processing considering LCA methodology as an innovation strategy in the Agri-food sector. Sustainability 10:979

Assiry AM, Sastry SK, Samaranayake CP (2006) Influence of temperature, electrical conductivity, power and pH on ascorbic acid degradation kinetics during ohmic heating using stainless steel electrodes. Bioelectrochemistry 68:7–13

Beattie JM, Lewis FC (1925) The electric current (apart from the heat generated) a bacteriological agent in the sterilization of milk and other fluids. J Hyg 24:123–137

Bobinaitė R, Pataro G, Lamanauskas N, Šatkauskas S, Viškelis P, Ferrari G (2015) Application of pulsed electric field in the production of juice and extraction of bioactive compounds from blueberry fruits and their by-products. J Food Sci Technol. https://doi.org/10.1007/s13197-014-1668-0

Bockris JOM, Reddy AKN, Gamboa-Aldeco M (2002) The electrified interface. In: Bockris JOM, Reddy AKN, Gamboa-Aldeco M (eds) Modern electrochemistry 2A. Fundamentals of electrodics. Kluwer Academic Publishers, New York, pp 771–1015

Bushnell AH, Clark RW, Dunn JE, Lloyd SW (1995a) Prevention of electrode fouling in high electric field systems for killing microorganisms in food products. United States Patent, US 5,393-541

Bushnell AH, Clark RW, Dunn JE Lloyd SW (1995b) Prevention of electrochemical and electrophoretic effects in high-strength-electric-field pumpable-food-product treatment systems. United States Patent, US 5,447-733

CODEX STAN 193-1995. http://www.fao.org/fao-who-codexalimentarius/codex-texts/tr/

CODEX STAN 247-2005. www.fao.org/input/download/standards/10154/CXS_247e.pdf

Donsì G, Ferrari G, Pataro G (2007) Inactivation kinetics of Saccharomyces cerevisiae by pulsed electric fields in a batch treatment chamber: the effect of electric field unevenness and initial cell concentration. J Food Eng 78:784–792

Donsì F, Ferrari G, Pataro G (2010) Applications of pulsed electric field treatments for the enhancement of mass transfer from vegetable tissue. Food Eng Rev 2:109–130

Dunn JE, & Pearlman JS (1987) Methods and apparatus for extending the shelf life of fluid food products. United States Patent, vol. US 4,695,472, 09/22

European legislation on the quality of water intended for human consumption for drinking water. (Directive No 98/83/EG). http://ec.europa.eu/environment/water/water-drink/legislation_en.html

Evrendilek GA, Dantzer S, Li WR, Zhang QH (2004) Pulsed electric field processing of beer: microbial, sensory, and quality analyses. J Food Sci 69:228–232

Fetterman JC (1928) The electrical conductivity method of processing milk. Agric Eng 9(4):107–108

Fauster T, Schlossnikl D, Rath F, Ostermeier R, Teufel F, Toepfl S, & Jaeger H (2018) Impact of pulsed electric field (PEF) pretreatment on process performance of industrial French fries production. Journal of Food Engineering, 235, 16–22

Gad A (2014) A study of electrode material performance during food processing by pulsed electric fields. PhD thesis. University of Waterloo, Waterloo, ON, Canada

Gad A, Jayaram SH (2011) Electrode material migration during Pulsed Electric Field (PEF) treatment. In: Conference ESA annual meeting on electrostatics 2011, Cleveland, Ohio, USA, pp 1–9. http://www.electrostatics.org/esa2011proceedings.html

Gad A, Jayaram SH (2012a) Effect of electric pulse parameters on releasing metallic particles from stainless steel electrodes during pulsed electric field processing of milk. In: Conference electrostatics joint conference 2012, Cambridge, ON (Canada), pp 1–7. http://www.electrostatics.org/esa2012proceedings.html)

Gad A, Jayaram SH (2012b) Effect of food composition and pH on electrode material migration during PEF application. In: conference BFE 2012, International conference bio & food electrotechnologies, Salerno, Italy, pp 49–52

Gad A, Jayaram SH (2014) Effect of electric pulse parameters on releasing metallic particles from stainless steel electrodes during PEF processing of milk. IEEE Trans Ind Appl 50(2):1402–1409. https://doi.org/10.1109/TIA.2013.2278424

Gad A, Jayaram SH, Pritzker M (2014) Performance of electrode materials during food processing by pulsed electric fields. IEEE Trans Plasma Sci 42(10):3161–3166. https://doi.org/10.1109/TPS.2014.2312711

Gileadi E (1993a) The ionic double-layer capacitance Cdl. In: Gileadi E (ed) Electrode kinetics for chemists, chemical engineers, and material scientists. VCH Publishers, New York, pp 185–224

Gileadi E (1993b) Electrode kinetics: some basic concepts. In: Gileadi E (ed) Electrode kinetics for chemists, chemical engineers, and material scientists. VCH Publishers, New York, pp 51–57

Gileadi E (1993c) Experimental techniques. In: Gileadi E (ed) Electrode kinetics for chemists, chemical engineers, and material scientists. VCH Publishers, New York, pp 349–454

Gilliland SE, Speck ML (1967) Mechanism of the bactericidal action produced by electrohydraulic shock. Appl Microbiol 15:1038–1044

Góngora-Nieto MM, Sepúlveda DR, Pedrow P, Barbosa-Cánovas GV, Swanson BG (2002) Food processing by pulsed electric fields: treatment delivery, inactivation level, and regulatory aspects. Lebensmittel-Wissenschaft Und-Technologie 35:375–388

Góngora-Nieto MM, Pedrow PD, Swanson BG, Barbosa-Cánovas GV (2003) Impact of air bubbles in a dielectric liquid when subjected to high electric field strengths. Innov Food Sci Emerg Technol 4:57–67

Jaeger H, Meneneses N, Knorr D (2009) Impact of PEF treatment inhomogeneity such as electric field distribution flow characteristics and temperature effects on the inactivation of *E. coli* and milk alkaline phosphatase. Innov Food Sci Emerg Technol 10:470–480

Jalte M, Lanoiselle JL, Lebovka N, Vorobiev E (2009) Freezing of potato tissue pretreated by pulsed electric fields. Food Sci Technol 42(2):576–580

Jeyamkondan S, Jayas DS, Holley RA (1999) Pulsed electric field processing of foods: a review. J Food Prot 62(9):1088–1096

Kempkes M (2017) Industrial pulsed electric field systems. In: Miklavcic D (ed) Handbook of electroporation. Springer, Cham, pp 1–21. https://doi.org/10.1007/978-3-319-26779-1_211-1

Kotnik T, Miklavčič D, Mir LM (2001) Cell membrane Electropermeabilization by symmetrical bipolar rectangular pulses. Part II. Reduced electrolytic contamination. Bioelectrochemistry 54:91–95

Kotnik T, Kramar P, Pucihar G, Miklavčič D, Tarek M (2012) Cell membrane electroporation — Part 1: The phenomenon. IEEE Electrical Insulation Magazine, 28(5), 14–23

Krüger S (1893) Über den Einfluss des constanten elektrischen Stromes auf Wachsthum und Virulenz der Bakterien. Zeitschrift klinische Medizin 22:191–207

Kim M, Zhang HQ (2011) Improving Electrode Durability of PEF Chamber by Selecting Suitable Material. In Nonthermal Processing Technologies for Food, H. Q. Zhang, G.V. Barbosa-Cánovas, V.M. Balasubramaniam, C.P. Dunne, D.F. Farkas, and J.T.C. Yuan (Ed.s), pp (201-212), Blackwell Publishing Ltd. and Institute of Food Technologists, Chichester, United Kingdom

Master AM, Schuten HJ, Mastwijk HC (2007) In Lelieveld HLM, Notermans S, de Haan SWH (eds) Food preservation by pulsed electric fields. CRC Press, New York, pp 201–211

Mastwijk HC (2007) Pulsed power systems for PEF in food industry. In: Raso J, Heinz V (eds) Pulsed electric fields technology for the food industry. Springer, New York, pp 223–237

Meneses N, Jaeger H, Knorr D (2011) pH-changes during pulsed electric field treatments – Numerical simulation and in situ impact on polyphenoloxidase inactivation. Innov Food Sci Emerg Technol 12:499–504

Morren J, Roodenburg B, de Haan SWH (2003) Electrochemical reactions and electrode corrosion in pulsed electric field (PEF) treatment chambers. Innov Food Sci Emerg Technol 4:285–295

Pareilleux A, Sicard N (1970) Lethal effects of electric current on *Escherichia coli*. Appl Microbiol 19(3):421–424

Parniakov O, Lebovka N, Bals O, Vorobiev E (2015) Effect of electric field and osmotic pre-treatments on quality of apples after freezing-thawing. Innov Food Sci Emerg Technol 29:23–30

Parniakov O, Bals O, Lebovka N, Vorobiev E (2016a) Effects of pulsed electric fields assisted osmotic dehydration on freezing-thawing and texture of apple tissue. J Food Eng 183:32–38

Parniakov O, Bals O, Lebovka N, Vorobiev E (2016b) Pulsed electric field assisted vacuum freeze-drying of apple tissue. Innov Food Sci Emerg Technol 35:52–57

Pataro G, Ferrari G (2020) Limitations of pulsed electric field utilization in food industry. In: Barba F, Parniakov O, Wiktor A (eds) Pulsed electric field to obtain healthier and sustainable food for tomorrow. Academic Press, London, pp 283–310

Pataro G, Senatore B, Donsi G, Ferrari G (2011) Effect of electric and flow parameters on PEF treatment efficiency. J Food Eng 105:79–88

Pataro G, Donsì G, Ferrari G (2012) Metal release from stainless steel electrodes of a PEF treatment chamber. In: International conference Bio & Food Electrotechnologies (BFE2012), Salerno, Italy, pp 29–33. ISBN 978-88-903261-8-9

Pataro G, Falcone M, Donsì G, Ferrari G (2014a) Metal release from stainless steel electrodes of a PEF treatment chamber: effects of electrical parameters and food composition. Innov Food Sci Emerg Technol 21:58–65

Pataro G, Barca GMJ, Pereira RN, Vicente AA, Teixeira JA, Ferrari G (2014b) Quantification of metal release from stainless steel electrodes during conventional and pulsed Ohmic heating. Innov Food Sci Emerg Technol 21:66–73

Pataro G, Barca GMJ, Donsì G, Ferrari G (2015a) On the modeling of electrochemical phenomena at the electrode solution interface in a PEF treatment chamber: methodological approach to describe the phenomenon of metal release. J Food Eng 165:34–44

Pataro G, Barca GMJ, Donsì G, Ferrari G (2015b) On the modelling of the electrochemical phenomena at the electrode solution interface of a PEF treatment chamber: effect of electrical parameters and chemical composition of model liquid food. J Food Eng 165:34–44

Pataro G, Donsì G, Ferrari G (2017a) Modeling of electrochemical reactions during pulsed electric field treatment. In: Miklavcic D (ed) Handbook of electroporation. Springer, Cham, pp 1–30. https://doi.org/10.1007/978-3-319-26779-1_5-1

Pataro G, Donsì G, Ferrari G (2017b) Modeling of electrochemical reactions during pulsed electric field treatment. In: Miklavcic D (ed) Handbook of electroporation. Springer, Cham, pp 1–30. https://doi.org/10.1007/978-3-319-26779-1_5-1

Pataro G, Carullo D, Falcone M, Ferrari G (2020) Recovery of lycopene from industrially derived tomato processing byproducts by pulsed electric fields-assisted extraction. Innov Food Sci Emerg Technol 63:102369

Prochownick L, Spaeth F (1890) Über die keimtötende Wirkung des galvanischen Stroms. Dtsch Med Wochenschr 26:564–565

Raso J, Frey W, Ferrari G, Pataro G, Knorr D, Teissie J, Miklavčič D (2016) Recommendations guidelines on the key information to be reported in studies of application of PEF technology in food and biotechnological processes. Innov Food Sci Emerg Technol 37:312–321

Rodaitė-Riševičienė R, Saule R, Snitka V, Saulis G (2014) Release of iron ions from the stainless steel anode occurring during high-voltage pulses and its consequences for cell electroporation technology. IEEE Trans Plasma Sci 42(1):249

Roodenburg B, de Haan SWH, van Boxtel LBJ, Hatt V, Wouters PC, Coronel P, & Ferreira JA (2010) Conductive plastic film electrodes for Pulsed Electric Field (PEF) treatment—A proof of principle. Innovative Food Science and Emerging Technologies, 11, 274–282

Roodenburg B, Morren J, Berg HE, de Haan SWH (2005a) Metal release in a stainless steel Pulsed Electric Field (PEF) system. Part I. Effect of different pulse shapes; theory and experimental method. Innov Food Sci Emerg Technol 6:327–336

Roodenburg B, Morren J, Berg HE, de Haan SWH (2005b) Metal release in a stainless steel pulsed electric field (PEF) system. Part II. The treatment of orange juice; related to legislation and treatment chamber lifetime. Innov Food Sci Emerg Technol 6:337–345

Sale AJH, & Hamilton WA (1967) Effects of high electric fields on microorganisms I. Killing of bacteria and yeast. Biochimica Biophysica Acta, 148, 781–788

Saldaña G, Álvarez I, Condón S, Raso J (2014) Microbiological aspects related to the feasibility of PEF technology for food pasteurization. Crit Rev Food Sci Nutr 54(11):1415–1426

Saulis G, Rodaitė-Riševičienė R, Snitka V (2007) Increase of the roughness of the stainless-steel anode surface due to the exposure to high-voltage electric pulses as revealed by atomic force microscopy. Bioelectrochemistry 70:519–523

Soliva-Fortuny R, Balasa A, Knorr D, Martín-Belloso O (2009) Effects of pulsed electric fields on bioactive compounds in foods: a review. Trends Food Sci Technol 20:544–556

Sun J, Bai W, Zhang Y, Liao X, Hu X (2011) Effects of electrode materials on the degradation, spectral characteristics, visual colour, and antioxidant capacity of cyanidin-3-glucoside and cyanidin-3-sophoroside during pulsed electric field (PEF) treatment. Food Chem 128(3):742–747

Thiele H, Wolf K (1899) Über die Einwirkung des elektrischen Stroms auf Bakterien. Centralblatt Bakterien und Parasitenkunde 25:650–655

Toepfl S, Heinz V, Knorr D (2007) High intensity pulsed electric fields applied for food preservation. Chem Eng Process 46(6):537–546

Tzedakis T, Basseguy R, Comtat M (1999) Voltammetric and coulometric techniques to estimate the electrochemical reaction rate during ohmic sterilization. J Appl Electrochem 29(7):821–828

U.S. Environmental Protection Agency (EPA), National Primary Drinking Water Regulations. https://www.epa.gov/ground-water-and-drinking-water/nationalprimary-drinking-water-regulations

U.S. Environmental Protection Agency (EPA), National Drinking Water Regulations, 2009. Secondary drinking water standards: guidance for nuisance chemicals. https://www.epa.gov/sdwa/secondary-drinking-water-standards-guidance-nuisance-chemicals

U.S. Food and Drug Administration (USDA) (2018) Guidance for industry: action levels for poisonous or deleterious substances in human food and animal feed. https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-action-levels-poisonous-or-deleterious-substances-human-food-and-animal-feed

Wiktor A, Iwaniuk M, Sledz M, Nowacka M, Chudoba T, Witrowa-Rajchert D (2013) Drying kinetics of apple tissue treated by pulsed electric field. Dry Technol 31(1):112–119

Zhao W, Yang R, Liang Q, Zhang W, Hua X, Tang Y (2012) Electrochemical reaction and oxidation of lecithin under Pulsed Electric Fields (PEF) processing. J Agric Food Chem 2012(60):12204–12209