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Editorial

A personal perspective on the role of electrochemical science and technology in solving the challenges faced by modern societies

1. Introduction

The fast growth of human population on planet Earth comes inevitably accompanied by the challenge of both maintaining the high living standards of developed countries, and extending them to developing economies. The first three problems associated to trying to reach these goals that probably come to mind are (i) producing enough food and ensuring water supply for all the population on earth, (ii) providing them with adequate health care, and (iii) generating enough energy to keep our strongly energy-consuming modern societies functioning, all this with a minimum impact on the natural environment.

The third of these points, i.e., energy conversion and storage, certainly occupies a central role in addressing these issues, as illustrated in Fig. 1, because energy is required in every human activity (from food production and extraction of raw materials, to the most modern information technologies), and because energy conversion is certainly the main source of residues generated by humanity (including CO_2 emissions held responsible for global warming). Almost all the energy available on our planet is of solar origin, the only exceptions being gravitational energy due to Earth's own mass, and nuclear energy stored in the form of unstable isotopes. With an average of 4×10^6 EJ year^{-1}, in approximately 53 min of daylight the sun provides the energy consumed by the entire human population in one year [1]. Obviously, the first problem to be faced is how to convert efficiently this overwhelmingly large amount of energy into a usable form (essentially, electricity). But equally important, due to the discontinue nature of renewable energy sources, is to find an efficient way to store this energy and deliver it when needed.

A consequence of addressing the three problems indicated above is the degradation of our natural environment. Even in the absence of industrial activity, the sheer size of human population would make dealing with the product of our metabolic activity a serious problem. Like that of any other organism, the metabolism of every single human being generates organic residues. Food production also generates a huge amount of residues, not only due to the use of fertilizers and pesticides, but also due to animal waste. In addition, antibiotics and other drugs are released in toxic amounts to the environment through the urine and feces of both human and domestic animals. Use of renewable energy sources, and the development of green industrial processes and more environmentally friendly drugs, fertilizers, etc., can contribute to solve the problem, but decreasing the amount of metabolic human and domestic-animals waste is not possible. Besides, decreasing the residues associated with agricultural activity would probably come at the cost of decreasing the amount of food produced. There is, hence, a necessity to detect and quantify all these contaminants, as well as of degrading them to innocuous final products.

One last problem which we would like to highlight is corrosion, a spontaneous reaction leading yearly to the waste of 2–4% of the world's GDP (between US$1.4 and 2.8 trillion out of ca. US$72 trillion). This compares with the Brazilian GDP (ca. US$1.9 trillion, the world's 9th). Good news is that ca. 40% of this value can be saved by preventive action, which of course demands for an increase in the knowledge of the process mechanism and velocity.

In this article we intend to discuss on how electrochemical science and technology can contribute to solving these problems. We are aware that many of the facts discussed here will appear as well-known or evident to some of the readers, but we believe nonetheless that it is worth to bring these issues to discussion from time to time.

2. What makes electrochemical devices and technologies attractive?

Electrochemistry can be defined as the science that studies the direct conversion of chemical energy into electrical energy, and vice versa. This is also what distinguishes electrochemistry from conventional chemistry, in which heat is used to drive chemical changes, or chemical changes are employed to generate heat. This essential difference between electrochemistry and conventional chemistry is similar to that characterising photochemistry, in which light substitutes heat, and their combination has made of photoelectrochemistry a very active research field.

The possibility of direct conversion between chemical energy and electrical work is arguably the most relevant of the characteristics that make electrochemical energy conversion technologies attractive. Any other alternative involves first converting chemical energy into heat and then using a thermal engine to convert the heat released into mechanical work, which can then be converted to electricity, by transferring the heat from a hot to a cold reservoir. According to the 2nd law of thermodynamics, the efficiency of such a thermal engine can never surpass that of an engine operating with a Carnot cycle, given by $\eta = 1 - \frac{T_c}{T_h}$, where T_c is the temperature of the cold reservoir and T_h is that of the hot reservoir in K.

As an example, the gas mixture inside the cylinder of an internal combustion engine reaches temperatures of up to 2480 K (T_h), and leaves the cylinder as exhaust at ca. 650 K (T_c). The absolute limit to the efficiency that can be achieved by an internal combustion engine is, hence of ca. 70%. Internal combustion engines obviously do not operate according to the ideal Carnot cycle, and actual efficiencies are significantly lower, around 35–40% for gasoline and 40–45% for diesel (please note that this efficiency is usually expressed as the fraction of ΔH of the reaction converted to work). This is mainly due to the fact that the materials used to build the cylinders cannot resist the high temperatures

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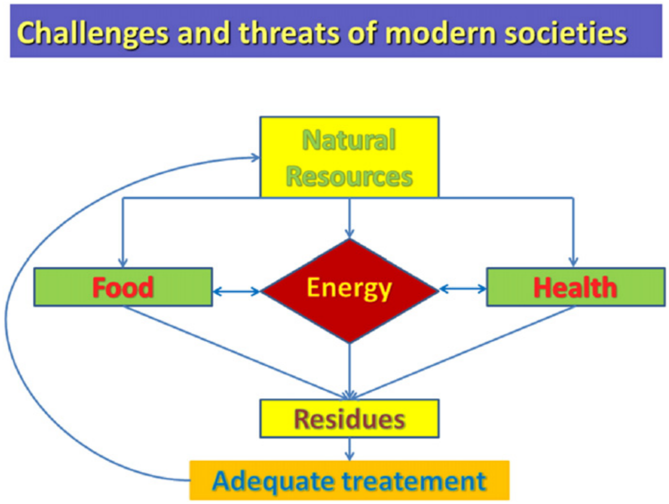

Fig. 1. The central role of energy in all human activities, and of energy conversion and storage in solving the most important threats and challenges faced by modern societies.

reached by the gas mixture [2], and have to be cooled down. As a consequence, the gas also cools down before expanding and escaping the cylinder to the exhaust, and all the heat lost is energy that cannot be converted to work. Attempts have been made to use ceramic materials [3], so that higher temperatures can be achieved and Carnot's limit be approached, but the fragility of these materials and the cost involved in their conformation and processing limits their implementation.

On the contrary, the theoretical efficiency of an electrochemical energy-conversion device is of 100% of ΔG. Referred to ΔH, the efficiency of an electrochemical energy-conversion device can be >100% if $\Delta S > 0$ (in the case of a hydrogen fuel cell, considering the formation of water vapour at 298 K, $\Delta G = -228.6$ kJ mol^{-1} and $\Delta H = -241.8$ kJ mol^{-1}, so the maximum, ideal efficiency, is of ca. 94% of ΔH). In summary, electrochemical energy conversion and storage devices are intrinsically highly efficient, and, for the same amount of work, result in lower emissions or, depending on the fuel, no emission of pollutants at all.

The arguments above lead to an interesting conclusion regarding the way in which living organisms convert energy, which is worth discussing here. Living organisms are highly efficient converting chemical energy. For example, mitochondria synthesize ATP (the main energy vector within cells) with an efficiency between 60 and 90% [4–6]. If we take the temperature in our body (309.65 K) as T_h, and ambient temperature (let's say 293.15 K) as T_c, the maximum efficiency achievable by a thermal engine would be 5% (actually, the temperature of mitochondria or unicellular organisms is essentially that of their surroundings, so the actual scenario is even worse. In warm countries where temperatures can reach over 40 °C in summer, assuming that we convert energy via a thermal process would imply a violation of the 2nd Law of Thermodynamics). The only alternative to a thermal engine is an electrochemical one, so we can conclude that living organisms are electrochemically powered systems (Fig. 2). This includes photosynthesis, a photoelectrochemical process in which, instead of harnessing the energy delivered when high-energy electrons in, e.g., glucose, are transferred to oxygen, solar energy is used to generate high-energy electrons that are then transferred to CO_2. These ideas were already suggested by Bockris and Tunuli 36 years ago [7], but lacking the thermodynamics-based argument, which is a long-held rationale of Gutiérrez's [8].

Coming back to our main discussion, the possibility to combine electrochemical reactions with light in photoelectrocatalytic processes, allowing to store both electrical and solar energy into chemical energy, is also highly attractive. As a consequence, the search for high-efficiency, low-cost photoelectroelectrochemical cell materials is an area of intense research. Electrochemistry also provides a conceptual framework in the area of photocatalytic conversion of solar energy, because heterogeneous photocatalytic processes are all of electrochemical nature [9], and a good understanding of electron transfer at electrochemical interfaces is required. Conceptually, the mechanism of photocatalysis is similar to that of corrosion in that separation of the photogenerated hole and electron creates short-circuited anodic and cathodic regions, respectively, on the photocatalyst surface [9].

Taking all of the above into account, it is no surprise that, in addition to being already present in our daily life, e.g., powering our laptops, cell-phones or tablets, electrochemical technologies are at the heart of current visions of a sustainable future based on the use of energy from renewables (Fig. 3). Solar energy or electricity from renewables can be stored as fuels using photo- and photoelectrocatalysis or electrolysers, respectively, and be later converted back to energy using fuel cells. Electricity from renewables can also be stored in a battery or a supercapacitor, and be released when needed. The implementation of an economy based on such a landscape would constitute a revolution, leading to a new technological ecosystem, but it confronts, not only new technological developments and reasonable concerns regarding what can be realistically achieved [10], but also a change in the way that energy is generated and distributed, as well as in the kind of economic relationships within our societies.

In addition to energy conversion and storage applications, electrochemical technologies are also attractive for other purposes. As analytical tools, electrochemical devices are very sensitive and allow detection at low concentrations, benefitting from the simplicity, accuracy and precision with which voltages and currents can be measured. Traditionally, the problem of selectivity has been addressed by combining electrochemical sensors with separation techniques, or by surface modification. However, application of chemometric techniques to electrochemical sensors could represent a change of paradigm, as has been the case before with other, non-electrochemical, analytical methods.

Similarly, decontamination of soils and water using electrochemical methods is an attractive alternative, among other reasons, because they allow to generate highly reactive species like chlorine, ozone or OH radical (the basis of the Fenton reaction) locally and in the amounts needed, thus avoiding transporting and storing potentially dangerous chemicals, or overdosing these reactive species, which can lead to unwanted toxic products via side reactions. In addition, electrochemical processes are faster than the commonly used biological processes, and have smaller spatial requirements.

3. What are the difficulties associated to deploying electrochemical devices and technologies?

Probably the most important electrochemical technologies in use, in terms of volume of product and energy consumed, are the chlor-alkali process and the primary production of aluminium. Annual production of chlorine is over 50 MTonnes, consuming between 2.5 and 3.4 MWh/Tonne of chlorine (depending on the technology employed), and that of aluminium slightly below 5 MTonnes, consuming ca. 14 MWh/Tonne of aluminium. This adds up to ca. 10 billionth of the world's annual electrical energy consumption (ca. 1×10^4 TWh in 2007 [1]). (We would like to note here that, unless the outdated mercury process is used, large amounts of hydrogen are produced as a valuable by-product in the chlor-alkali process. Recycling this hydrogen with a fuel cell to provide part of the electricity required by the chlor-akali plant can reduce the costs of the process and the associated CO_2 emissions [11].)

Electrolysis is also used in the production of permanganate and in the on-site production of AsH_3 for the electronics industry, in the extraction, refining, fabrication and finishing of metals, and in the fabrication of electronic components. Widely-employed glucose sensors are also electrochemical, and cathodic and anodic protection, as well as sacrificial anodes, are common in corrosion control.

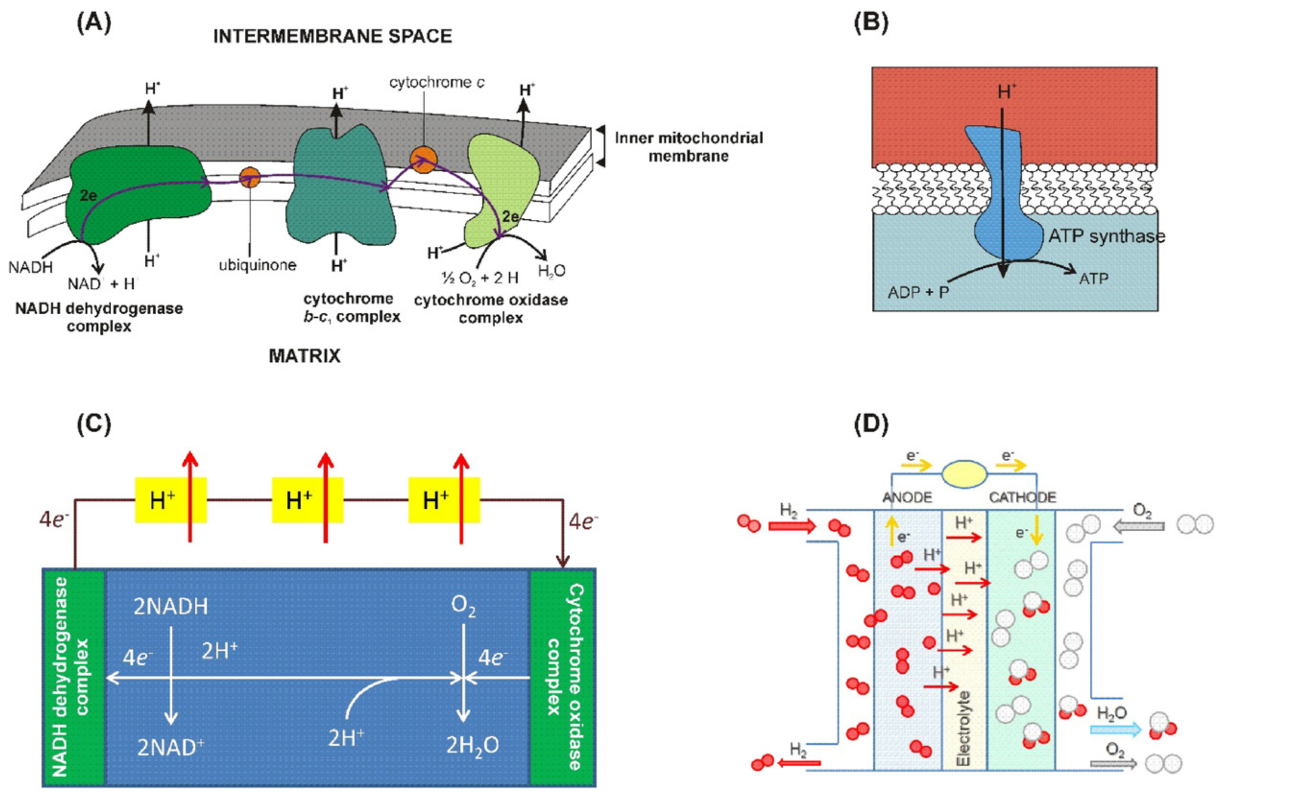

Fig. 2. Energy conversion in mitochondria (A). NADH is oxidised by the NADH dehydrogenase complex, and the electrons are transported along a chain of redox centres embedded in the inner mitochondrial membrane, until finally being transferred to O_2 by the cytochrome oxidase complex. The energy released as the electrons travel downhill the electrostatic potential is employed to pump H^+ from the mitochondria's matrix into the intermembrane space, which can be considered as charging an (electro)chemical capacitor. The energy released when this capacitor is discharged, by allowing the protons to flow downhill their electrochemical gradient, is used by ATP synthase to phosphorylase ADP to ATP (B), which can then be used as an energy vector by the cell. A simple schematic diagram (C), allows to visualise the analogy between the energy conversion process in (A) and that in a fuel cell (D), with the NADH dehydrogenase complex and the cytochrome oxidase complex playing the roles of anode and cathode, respectively, the matrix acting as the electrolyte, the chain of redox centres in the inner mitochondrial membrane acting as the electronic conductor connecting anode with cathode, and the proton pumps playing the role of the load in the electrical circuit.

However, although there are also commercial electrochemical technologies available for the synthesis of many inorganic and organic chemicals, for the recycling of chemicals and process streams, for the purification and separation of chemicals, for water and effluent treatment, for the total destruction of toxic materials and soil remediation, etc., most of these applications are dominated by other type of technologies. In particular, in the case of energy conversion and storage, we are far away from the idyllic landscape outlined in Section 2.

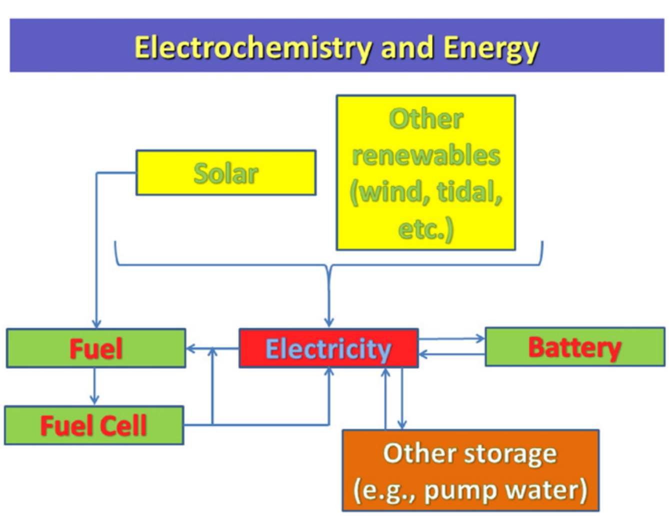

Fig. 3. The particularly relevant role of electrochemical energy conversion and storage technologies in an eventual sustainable economy.

If electrochemical devices and technologies are as efficient as described above, and so attractive for different purposes, why is their presence not more widespread? An obvious answer is that neither electrochemistry, nor any other technology, can be the panacea to all of our problems and challenges. At the end of the day, it is economic factors (essentially, the cost of the materials and of the process itself, which will be largely determined by its efficiency) what will determine which technology will be deployed for a given application. In the case of electrochemical processes and devices, the cost of electricity is an obviously important factor, and we need to distinguish between two sides of the same coin:

1. The cost of the electricity necessary to drive an electrochemical process (e.g., the primary production of Al). As an example, assuming an energy efficiency (referred to ΔG) of 100%, producing 1 kg of H_2 via electrolysis at atmospheric pressure would require 66 kWh. The cost of the industrial kWh is of ca. €0.120 in Europe (EU-28 averaged, figures from 2014 [12]), and of US$0.0701 in the US (figures from 2014 [13]). This results in a minimum cost per kg of H_2 from electrolysis of between US$4.6 and US$8.85. Every 123 mV increase of the operating cell potential over the ideal open-circuit potential of 1.23 V (at which current, and, hence, H_2 production, is zero) will imply a 10% increase of these figures. For the sake of comparison, the price of hydrogen from reformate is less than US$5 per kg of H_2 [14]. The practical consequence of this is that, traditionally, electrolytic methods have only been used for the production of chemical commodities when there was no other method available, as in the case of the chlor-alkali process or of the production of aluminium mentioned above, which are still, by large, the most important industrial electrochemical processes. Please note that the prices given

above correspond to the current energy mix, largely dominated by the use of fossil fuels. Electricity from wind or solar is currently more expensive, before incentives, and would add to the final cost.

2. The cost of the electricity produced with, or stored in, an electrochemical device (e.g., a fuel cell or a battery, respectively). Leaving aside the cost of materials, which will be discussed below, the cost of the fuel used to feed a fuel cell, or the cost of the electricity we store in a battery, together with the efficiency with which this energy can be stored and released, will set a lower limit to the price of the electricity generated or released. If we use a hydrogen fuel cell to generate electricity, the cost will not be the same when using hydrogen from reformate or hydrogen from electrolysis using electricity from renewables (although the former would only contribute slightly, if at all, to reducing CO_2 emissions). If we use a battery to store excess electricity from renewables in order to use it when needed, the original price will also set a lower limit to the cost of electricity when released (actually, in this case the final price will be increased by the fact that, for the same current density, the voltage applied to charge our battery will always be larger than the voltage obtained when the energy is released).

The two points above only consider how the efficiency of an electrochemical device combines with either the cost of electricity, or with the price of the fuel used, to set a minimum to the final price of the product generated with an electrolyser, or to the electricity released by a fuel cell or a battery. But this will only be a fraction of the actual final cost. Among other contributions, particularly worth highlighting are:

1. The cost of the operating device. For example, in the case of polymer-electrolyte membrane fuel cells (PEMFC), one of the most likely candidates for powering electric vehicles in an eventual, hydrogen-based sustainable future economy, the amount of platinum needed as electrocatalyst, assuming a typical power of 100 kW, had been reduced in 2013 to 30 g per car [15] (0.3 g kW^{-1}, most of it in the cathode). At current prices (US$1078.80 per ounce = US$34.68 per gram, June 2015), this corresponds to ca. US$10.4 per kW, or US$1,040 worth of Pt per car. But this cost estimation is not completely realistic, because the world's reserves of Pt amount to only 66,000 Tonnes [16]. The annual production of Pt is currently estimated to be around 220 Tonnes, which would limit the number of fuel-cell powered vehicles fabricated per year (100 kW with state-of-the-art technology) to <4.5 million worldwide (well over 70 million passenger cars were produced in the world in 2014). The concentration of resources (95% of the Earth's Pt reserves located in South Africa) and the short supply, coupled with the expected increase in demand if the automotive industry shift from internal combustion- to FC-powered vehicles, is likely to cause Pt prices to rocket. With approximately 1.2 billion cars currently on our planet [17], were all of them to be substituted by vehicles powered with the current PEMFC technology, 36,000 Tonnes of Pt, i.e., 54.5% of all the known reserves, would be required. If the projections of 2 billion cars on our planet's roads by 2035 prove themselves correct, 60,000 Tonnes of Pt would be required to power them all with the current PEMFC technology, what would exhaust our reserves. A similar problem is faced by the deployment of Li or Li-ion batteries to power electric vehicles, or for stationary storage of electricity from renewables: despite being an abundant element, its reserves are limited (13.5 million Tonnes; the amount of Li in seawater is estimated to be around 230 billion Tonnes, but the cost of extracting it would be prohibitive) and concentrated (55% of them in Chile and 26% in China [18]).
2. The durability of the materials. Even if materials with an excellent cost to efficiency ratio are developed to be used as electrodes in electrochemical processes, the cost of the latter would increase considerably if these materials have to be replaced frequently, or if their degradation affects their efficiency. Operating electrochemical devices are more than just the electrode, and all the other elements must also be taken into account. In particular, degradation of the electrolyte during operation can increase considerably the internal resistance of an electrochemical cell, affecting the efficiency, and, hence, the cost, of the device and/or the process.
3. The change in infrastructure. Essentially in relation with the substitution of a fossil-fuel based economy by a combination of renewables with electrochemical energy conversion and storage. Currently, energy is essentially generated in large power stations, from which energy is distributed to the final consumer. Switching to a renewables-based economy will imply a transition to, or at least a combination with, a distributed generation system, in which smaller amounts of energy are generated and used locally, excess energy being either stored (where electrochemical technologies come into play) or released to the grid to be used elsewhere. The above-discussed development of renewable energy conversion and electrochemical energy conversion and storage systems with adequate cost/efficiency ratios and high durability, hence, will have to be accompanied by technically challenging changes in the grid infrastructure, as well as by societal changes.

4. What is necessary to overcome these limitations?

Overcoming the limitations highlighted in the preceding section requires a multidisciplinary approach, as well as the combination of fundamental and applied research, so that ground-breaking results from the former can find rapid practical implementation through the latter. Cross communication between those focused on understanding the deepest scientific foundations of electrochemical processes and those preoccupied by the engineering problems associated with their practical implementation, is utterly important. But both approaches need to be considered equally relevant: without a pragmatic approach, our advance in understanding the physical world around us will fail to be translated into new technologies, but focusing on the applications would close the way to qualitative, really transformational changes brought about by new knowledge.

Also necessary is an open mind that transcends the artificial limits between disciplines. The development of the technologies outlined above to a commercially competitive level will require input from fields as disparate as electrochemistry, materials science, solid-state physics and chemistry, photovoltaics, biological sciences, etc. However, in our opinion, the special relevance of electrochemistry lies in the fact that it is relevant per se, but also as a tool for the other disciplines involved. Furthermore, electrochemistry also provides the conceptual framework necessary to understand phenomena as complex as those underlying life itself, as discussed above.

5. Epilogue

Networking and bringing together researchers with different expertise and background, offering different perspectives on the same problems, is the way to tackling the complex challenges faced by humankind in the XXI century. The potential of such an interaction is enhanced if the illusion and creativity of young age is added to the cocktail. This was the underlying principle of the Workshop ElSol 2015, which, with the support of FAPESP and the British Council, brought together early-stage researchers from Brazil and the UK to discuss on the application of electrochemical science and technology to address those problems, and exchange their visions, ideas and results.

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Ernesto C. Pereira
Departamento de Química, Universidade Federal de São Carlos, São Paulo, Brazil
Corresponding author.
E-mail address: ernestopereira51@gmail.com

Angel Cuesta
Department of Chemistry, University of Aberdeen, AB24 3UE, UK
Corresponding author.
E-mail address: angel.cuestaciscar@abdn.ac.uk