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FEATURE ARTICLE

Future challenges in electrochemistry: linking membrane-based solar energy conversion mechanisms to water harvesting

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Electrochemical science challenges

As a short personal perspective, this feature article is written to capture a vision for electrochemistry as a subject fundamentally linked to energy conversion mechanisms. As such, electrochemistry will make considerable future impact, both academically and practically, in traditional and in emerging topics linked to energy and linked to new mechanisms for energy conversion (optical, chemical, mechanical, thermal, etc.). The field of electrochemical science is broad and diverse, and it offers fundamental and interdisciplinary challenges at many levels (which is linked also to educational challenges, e.g. at university level where electrochemistry often appears inaccessible to students and at professional development level where there is considerable demand for training courses [1]). Electrochemistry contributes to the development of technologies such as battery systems, (bio-)fuel cells, organic and inorganic materials electrosynthesis, electroanalysis, and solar-/photo-electrochemical systems including artificial photosynthesis. Many of these technologies are associated with complex multiphase electrochemical systems (which are challenging to unravel and understand at fundamental level). Both current state-of-the-art in situ imaging or spectroscopy tools and current state-of-the-art computational tools are still not sufficiently advanced for fully resolving or explaining/predicting many important phenomena, but a lot of progress is being made [2–4].

As a key contribution to analytical measurement tools, electrochemistry has now been able to reach the single entity and/or the single molecule domain [5]. Devices have been developed to detect single redox-active molecules or enzymes based on rapid feedback signal amplification between two very closely spaced electrodes in nanogaps or based on modulated ion transport in nanochannels [6]. The understanding and exploitation of electrochemical mechanisms in nanospaces or at nanoelectrodes remains an interesting and important challenge with opportunities. In electroanalytical sensing, new types of devices with multiple amplification strategies (based on nanostructures or based on molecular mechanisms) have been developed to probe extremely low concentrations in biological/health applications, e.g. for diagnostic microRNA in blood [7]. This field also presents formidable future challenges with many more crucial analytical targets in medicine and environmental analysis to be detected reliably and at low cost.

Mechanisms at electrode surfaces and in composite catalyst materials require nanoscale study and understanding to unravel the complexity in important electrocatalytic reactions, such as oxygen evolution or carbon dioxide reduction. Recent progress towards single nanoparticle electrocatalysis, for example, with MOF-derived oxygen evolution catalysts has been very revealing [8] in terms of true quantifiable catalyst particle behaviour. However, for practical applications, the microscopic catalyst performance is only one part of the factors affecting the overall system performance. There are many more criteria for technologies to become viable or competitive. Often challenges cannot be addressed solely by dissection.

Electrochemical processes occur not only at electrodes but also at membranes [9]. Potential-driven membrane processes are well-known in biology, where many transport phenomena as well as photosynthetic machinery are membrane-localized [10]. The key reason for processes being naturally associated with membranes is the interfacial energy conversion from electrochemical potentials to chemical and vice versa. Only at a membrane can electrochemical potential (notionally the sum of a chemical potentials and a term related to the interfacial Galvani potentials) gradients persist and be converted based on intriguingly complex mechanisms such as that reported for ATPases [11]. Therefore, artificial membrane

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systems could offer a wealth of future opportunity and challenges for electrochemical systems. Lewis, Freund, and coworkers reviewed recent progress in artificial energy conversion membrane mechanisms for solar energy harvesting and for electrolytic water splitting [12].

Figure 1 shows a classic four-electrode electrochemical measurement cell configuration for applying a bias voltage across a membrane. The working and sense electrodes on the right and the counter and reference electrode on the left provide control over potential or current and allow membrane processes to be studied. Here, the membrane is based on a microhole, e.g. a 20-μm diameter hole laser drilled into a polymer support (as introduced by Girault and coworkers [13]). The resulting experimental system offers microelectrode-like mass transport and steady-state electrochemical responses accessible at conventional time scales [14].

The measurement with an empty microhole and with symmetric electrolyte solution on both sides would result in Ohmic behaviour associated with the specific conductivity of the electrolyte [15]. When applying an ionomer such as Nafion [16] asymmetrically onto one side (see Fig. 1b), a new effect occurs: due to redistribution of electrolyte in the microhole region, semiconductor-diode-like "closed" and "open" states are observed at negative or positive bias, respectively. When creating a "junction" of Nafion with other porous materials, the effects can be enhanced and the mechanism modified [17]. When employing semipermeable ionomers such as Nafion, there are many nanochannels within this material to allow ion transport and ionic current rectification as defined by the material properties. Similar and more individually tuneable effects (with substantially lower currents) are observed also for single nanochannels with asymmetry in charge or shape [18, 19]. In contrast to conventional microelectrode processes, where electron transfer and redox chemical transformations occur, here at the asymmetrically modified microhole, primarily ion transport (either for cations or for anions) occurs unidirectionally. This can be exploited, for example, by combining two diodes in the AC-driven desalination of seawater [20]. In contrast to DC-driven electrolytic processes, the AC-driven mechanism can avoid external driver electrode side product formation and is therefore inherently less energy intensive. Could this or similar types of rectifier processes lead to new membrane mechanisms for solar energy conversion processes?

Membrane-based solar energy conversion mechanisms

In view of a global human population approaching 8 billion, it is important to ask what the future role of electrochemical science and technology could be to help ensuring supply of energy and food and water (all three are closely interconnected). The supply of water has to be seen as a truly global challenge. In his book on urbanization, Geoffrey West [21] highlighted the need for ever more rapid innovation and a need for technologies to become more sustainable and based on solar power as an obvious abundant energy source: "…the scale of solar energy is so vast that in one year it is about twice as much as will ever be obtained from all the Earth's nonrenewable resources of coal, oil, natural gas, and uranium combined". This should obviously happen in a fair way to provide benefits to everybody and not just a few. Could membrane (photo-)electrochemistry help provide power, food, and water in a sustainable manner?

As an interdisciplinary science, electrochemistry can benefit from a closer look at biological processes for guidance. Membrane processes in biology are ubiquitous and the key to many crucial processes: transmembrane ion transport, water

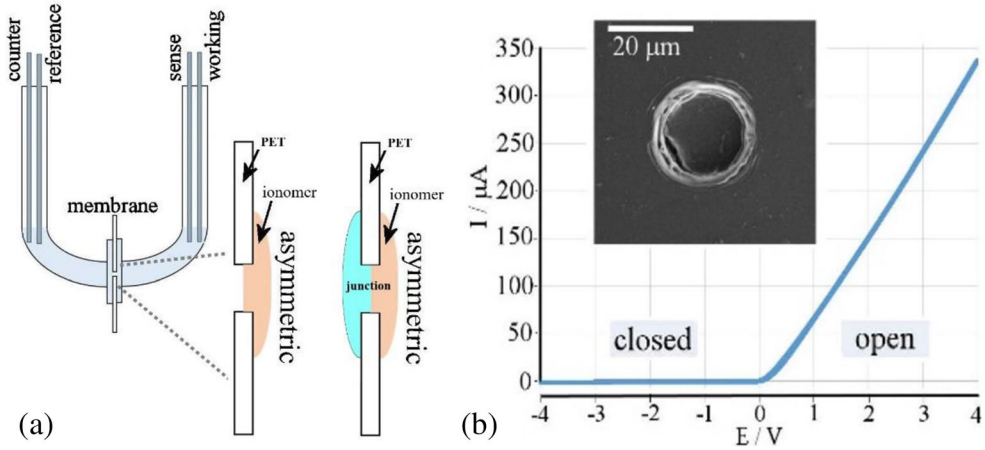

Fig. 1 **a** Four-electrode measurement cell for membrane electrochemistry with a microhole membrane either asymmetrically deposited or forming a junction with a second material on the opposite side. **b** Typical I–V curve (scan rate10 mV s^{-1}; aqueous 10 mM HCl on both sides), showing a closed and open diode. The inset shows an electron micrograph of the 20-μm diameter microhole filled with Nafion and imaged from the polyethylene terephthalate or PET side (reproduced with permission from [14])

transport, "hoovering" out of undesirable molecular species from within the cell [11], photoelectrochemical energy conversion, and electrical signalling/communication. Electrochemistry has been instrumental in unravelling the principles of bioenergetics [10, 22] and in analysing the function of many membrane components. Could this knowledge be the starting point for new types of membrane processes based on artificial materials and based on artificial mechanisms to mimic and advance some of the critical processes we need to water, power, and feed the population? Nature offers beautifully intricate and effective solutions to problems like water transport, for example, in the case of water-transporting channels such as aquaporins [23].

Let us envisage new types of membrane mechanisms may be with two non-equivalent ionic diodes working against each other: one diode "pumps" cations and water from one reservoir into another reservoir; the second diode "pumps" cations back but with a different amount of water cotransport. Combining the two diodes to operate simultaneously (in opposite direction) leads to zero net ion transport coupled to water pumping across membranes. This effect could avoid externally applied pressure as required in traditional water purification processes, and it could be powered by solar electricity. Similarly, membrane pump mechanisms could be developed for other types of neutral or charged molecules. In more complex energy conversion scenarios, transport of molecules across the membrane could be coupled to bipolar redox chemical conversions within the membrane, similar to those in bipolar electrochemistry in freely moving objects [24].

Externally applied solar electricity from photovoltaic panels will be commercially highly competitive as compared with more complex integrated technologies, as is the case for solar water splitting to hydrogen. However, it might also be possible to configure or design membrane mechanisms with a low-cost directly integrated solar electricity generation [12]. This will require light absorption, charge separation, interfacial redox reactions at opposite sides of the membrane, and associated unidirectional ion/molecular transport to balance the overall processes. Designing new materials and composite structures as well as new mechanisms to give effective artificial membranes with internal charge separation is a future challenge, but not impossible. The key here appears to be finding new integrated mechanisms, for example, by exploiting ionic diode phenomena. Nanoengineering of new materials will be required for this type of membrane development. Low-cost and sustainable materials will be desirable. In the (not too distant) future, solar-powered membranes could perform tasks like atmospheric water harvesting, irrigation for food production, carbon dioxide reduction and formation of solar fuels, or the treatment of polluted environments.

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