

Tracking Electrons - Colourful Insights into the Processes of Bipolar Electrochemistry with Polypyrrole

Dominik Quarthal, Marco Oetken *

¹Department of Chemistry, Physics, Technology and their teaching methodologies,
University of Education Freiburg, Kunzenweg 21, 79117 Freiburg, Germany,

*Corresponding author: marco.oetken@ph-freiburg.de

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Abstract The following article is intended to highlight the importance and usefulness of bipolar electrochemistry for science and for school and university teaching. In addition, a suitable explanation of the phenomena that take place on the basis of bipolar electrochemistry will be presented and visualised and confirmed by means of the different colours of the oxidation states of polypyrrole.

Keywords: bipolar electrochemistry, polymers, polypyrrole, water electrolysis

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1. Introduction

Bipolar electrochemistry is an important branch of electrochemistry. Unlike the conventional electrodes of an electrochemical cell, a bipolar electrode (BPE) has both oxidation at one end and reduction at the other. The bipolar electrode is located in the electric field of two 'normal' electrodes. In bipolar electrochemistry these are called working electrodes. The big advantage is that the BPE does not need to be in direct electrical contact, but only in the electrical field of two working electrodes. [1].

The fact that electrochemical reactions no longer require direct contact has many advantages, and bipolar electrochemistry is finding its way into normal application areas. Bipolar electrodes or bipolar plates are used in water electrolysis in polymer electrolyte membrane (PEM) fuel cells. The major advantage is that they reduce the electrical resistance of the fuel cell, increasing energy efficiency and improving heat dissipation and lifetime. By eliminating direct contact, the flow of hydrogen and oxygen can be optimised. This leads to a better current yield and higher efficiency of the fuel cell. [2].

Another major advantage of bipolar electrochemistry is the non-contact deposition of different materials on the BPE. This makes it possible to electrochemically deposit various polymers at the nanoscale, such as polypropylene, polyaniline and polythiophene. Not only is it easier to synthesise, but it is also possible to deposit polymers with a higher degree of purity. In addition, the polymer layers can be deposited so thinly on various substrates that more efficient electronic devices and sensors can be created [3].

In addition, the research group led by Salinas and Arnaboldi et al. summarised in their article that bipolar synthesis also allows the characterisation of the

electrochemical properties of conductive polymers, including conductivity, capacitance and carrier density [4].

The societal relevance of bipolar electrochemistry can be seen in many applications in materials science (e.g. in electrosynthesis, in the development of battery systems, in nanotechnology and also in medicine). For this reason, the working group of Fosdick, Knust et al. aimed in their review article on bipolar electrochemistry published in 2013 to introduce scientists from the fields of chemistry, physics and biology to the diverse (interdisciplinary) application possibilities as well as the mode of operation of this topic. [1].

With the current energy crisis and the need to save energy, the most important application of bipolar electrochemistry is probably in battery systems. The great advantage of using bipolar batteries is that space can be saved. Due to the smaller size of the housing components and the elimination of connecting elements, about half of the space required by a conventional battery can be saved. In 2018, the Fraunhofer IKTS succeeded in transferring the bipolar principle to the lithium-ion battery in its "Embratt-goes-FAB" project [5].

The working group at the Freiburg University of Education in the Department of Chemistry is concerned with preparing this topic in such a way that it can be implemented in school curricula, due to its topicality and presence in science.

The principle of bipolar electrochemistry is explained using the example of water electrolysis: Two electrodes are immersed in an aqueous electrolyte. When a sufficient external voltage is applied, oxygen is produced by chemical oxidation at the anode and hydrogen is produced by chemical reduction at the cathode. If an electrically conductive material is placed between the anode and cathode in the electrolyte, it can be seen that hydrogen and oxygen are also produced at the opposite ends of the

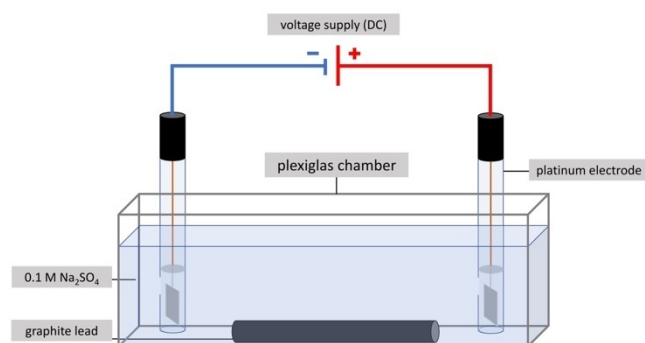


Figure 5. Schematic representation of the experimental set-up for gas evolution at a bipolar electrode. (here in the form of a pencil lead)

By applying a voltage, electrons are removed from the water molecules at the **+ pole**, forming oxygen molecules and oxonium ions (H_3O^+). The removed electrons are then transferred via a separate circuit to the **- pole**, where they are absorbed by the water molecules and reduced to hydrogen molecules and hydroxide ions (OH^-) (see Figure 6). To compensate for the difference in charge, the hydroxide ions diffuse to the **+ pole** and the oxonium ions diffuse to the **- pole**. This can be detected using suitable indicators. As a 0.1 M sodium sulphate solution was used in this experiment, Na^+ ions can also diffuse to the **- pole** and SO_4^{2-} ions to the **+ pole** to compensate for the difference in charge.

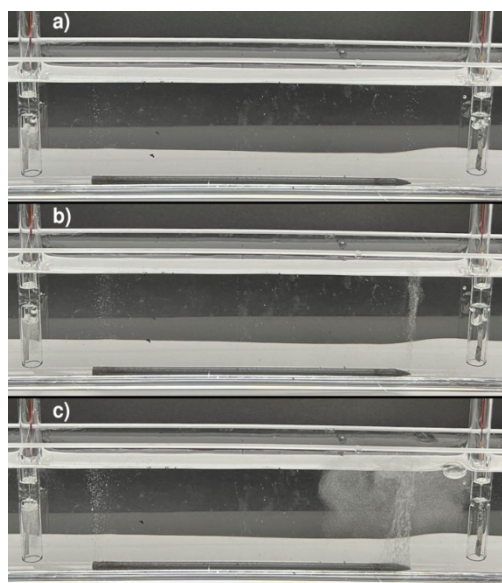
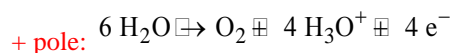
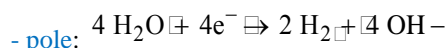


Figure 6. Gas evolution at the (platinum) driving electrodes and at the (graphite) bipolar electrode at a voltage of 15 V (a), 20 V (b) and 30 V (c)

The general reaction equations can be formulated in the following way:



We believe that the best way to explain the phenomena at the bipolar electrode to students is as follows:

By applying a voltage within the solution in the E-field between the platinum electrodes, anions are attracted by

the **+ pole** or repelled by the negative polarisation of the **- pole**. It is also possible that not only the anions of the solution but also the electrons of the bipolar electrode (here graphite) are attracted by the **+ pole** or repelled by the **- pole** (see (Figure 7)). As a result, the electrons in Figure 7 are shifted to the right side of the graphite electrode towards the **+ pole**. The attraction of the electrons from the **+ pole** now creates a charge difference within the graphite lead. The number of electrons increases on the right side of the lead and decreases on the left side (Figure 7).

If the voltage is now increased, the electron potential in the BPE increases, so that at very high voltages (here 15 V) the decomposition voltage U_z of water is exceeded (Figure 6) and the electrons on the right side of the graphite mine are released to the water molecules and the electrons of the H_2O molecules on the opposite side are taken up (see Figure 8).

The pencil lead should be polarised at low voltages before the water is decomposed at the bipolar electrode. The side facing the **+ pole** would have to be negatively polarised because the electrons migrate there due to the attraction of the **+ pole** and the repulsion of the **- pole**. To balance the charge, Na^+ ions should diffuse to the negatively polarised side and adsorb there. SO_4^{2-} ions should diffuse to the positively polarised side of the bipolar electrode and also adsorb there (see (Figure 7)). Accordingly, an electrical double layer should form, similar to supercapacitors (electrical double layer capacitors, EDLC). [9].

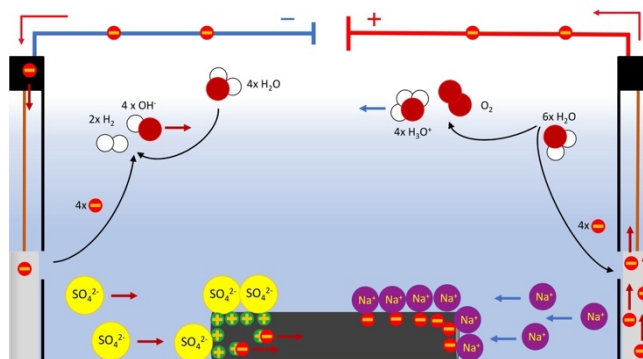


Figure 7. Schematic representation of the processes during the electrolysis of a 0.1 M sodium sulphate solution prior to reaching the decomposition voltage at the BPE.

Unfortunately, the movement of electrons within the BPE is not visible and we cannot easily detect it visually with graphite as the BPE. In order to be able to visualise the shift of electrons within a bipolar electrode, a conductive material would be needed that would change colour when accepting or releasing electrons. This would make it possible to create a bipolar electrode that changes colour as the electron density increases or decreases. To produce such a didactic "electron detector", the use of electrochromic materials was resorted to. One such suitable electrochromic material is polypyrrole.

The conductive polymer polypyrrole is of great interest in research. Because of its good conductivity, ease of production and high long-term stability, it is used in many technical products, such as "smart windows", as a counter-

electrode for electrical capacitors, as an electrode material in batteries, but also as a material for membranes [10]. The polymer is made from the monomer pyrrole.

For this reason, experiments are presented below in which polypyrrole is first produced on FTO glass by electrochemical polymerisation of pyrrole and the coated FTO glass is then used as BPE. The electrochemical deposition was carried out according to [11,12].

2. Experiments

2.1. Experiment 1: Electrochemical Deposition of Pyrrole

2.1.1. Equipment and Chemicals

Plastic vessel, voltmeter, ammeter, connecting cable, voltage source, alligator clips, Keratherm[®] graphite foil 4 cm 8 cm (source: www.conrad.de), FTO glass, 100 mL volumetric flask, distilled water, sodium dodecylbenzene sulphonate (NaDBS) (GHS05 - corrosive; GHS07 - harmful), pyrrole (98%) (GHS02 - flammable; GHS05 - corrosive; GHS06 - acute toxicity), acetone (GHS02 - flammable; GHS07 - irritant).

2.1.2. Preparation of Electrolyte Solutions

Prepare a 0.1 M pyrrole solution with 0.03 M NaDBS. Add 0.66 mL of pyrrole and 1.05 g of NaDBS to a 100 mL volumetric flask, fill with distilled water and stir with a magnetic stirrer until the conducting salt and the small amount of pyrrole are completely dissolved.

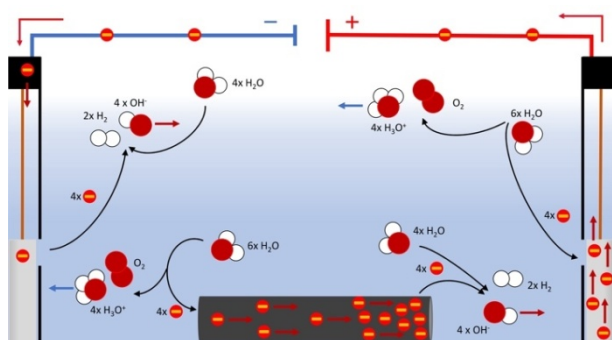


Figure 8. Schematic representation of the processes involved in the electrolysis of a 0.1M sodium sulphate solution at voltages above 19 V

2.1.3. Experimental Set-up

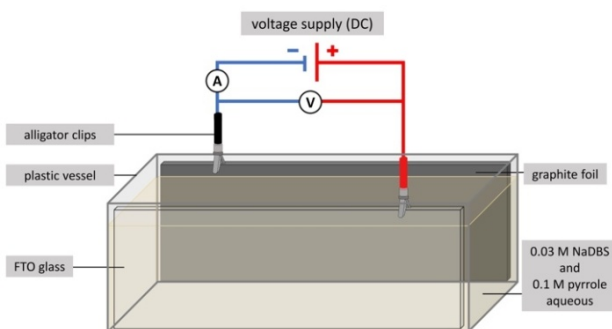


Figure 9. Schematic representation of the experimental set-up for the electrochemical deposition of polypyrrole.

2.1.4. Procedure

The two electrodes (graphite foil and FTO glass) are carefully cleaned with acetone. Then the conductive side of the FTO glass is determined with a multimeter and the experiment is set up as shown in Figure 9. The graphite foil is connected as the negative terminal and the FTO glass as the positive terminal. Ensure that the conductive side of the FTO glass faces the graphite foil. The electrodes are fixed to the upper edge of the vessel with an alligator clip. Apply a voltage of about 3 V. Electrolysis can be carried out for different lengths of time; the optimum electrolysis time is about 90 seconds.

A new FTO glass must be used for each electrolysis. The electrolyte and graphite foil can be used several times. After each electrolysis, the FTO glass is removed from the electrolyte and briefly immersed in a water bath. It is then placed on an absorbent cloth to dry.

2.1.5. Observation

The previously transparent FTO glass is uniformly covered with a black PPy layer after the electrolytic deposition process. The longer the electrolysis, the more intense the black colour. The optimum electrolysis time has been found to be 90 seconds, which gives a good ratio of layer thickness to transparency (Figure 10). If the electrolysis time is too long, this will result in low cycle stability in the subsequent electrochromic recolouration test. In addition, the colours of thicker layers cannot be observed as well as those of thinner layers.

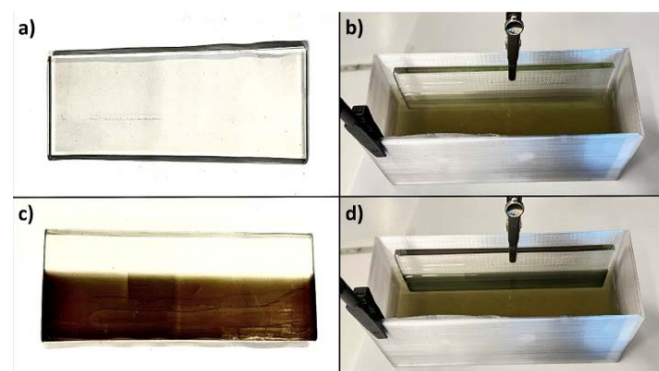


Figure 10. a) FTO glass uncoated. b) Apparatus for the electrochemical deposition of pyrrole before electrolysis. c) FTO glass coated with polypyrrole after 90 seconds, electrolysis at 3 V. d) Apparatus for the electrochemical deposition of pyrrole after an electrolysis time of 90 seconds

2.1.6. Explanation

PPy has been anodically deposited onto the FTO glass. Electrons are removed from the + pole and the pyrrole monomer is correspondingly oxidised or polymerised. The polymer polypyrrole is formed on the surface of the FTO glass. The initially neutral polymers are now further oxidised during anodic deposition and counter anions are doped into the PPy layer to balance the charge (p-doping, Figure 11).

In our case, the deposition electrolyte contains the dodecylbenzene sulphonate anion. By adding such a large macroanion, the electrochemical synthesis produces a stable polymer and a very uniform, smooth and transparent polypyrrole layer. The reaction equation for

electrochemical polymerisation and the associated oxidation (p-doping) can be formulated as follows:

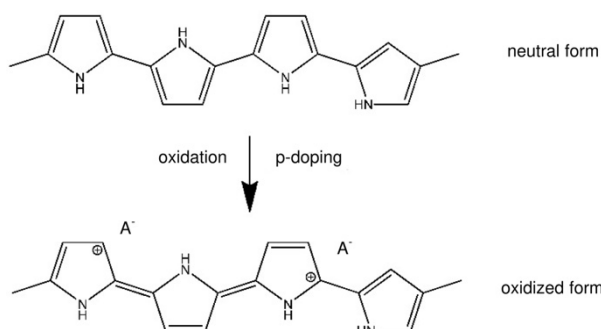
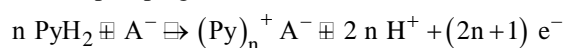


Figure 11. p-doping of the neutral polypyrrole polymer (A⁻: anion). Taken from [11].

This polypyrrole layer is now **black** in its oxidised form (PPy⁺DBS⁻). When electrons are added, this reduced form changes from **black** to **yellow** (PPy⁰DBS⁻Li⁺). As the colour changes from **black** to **yellow**, the mixed states or intermediates of polypyrrole appear **blue** and **brown-red**. Using polypyrrole as a bipolar electrode, the colouration would mean the following for our didactic "electron detector": If the electrons within the **black** polymer layer shift to one side, the side with the electron deficiency should appear **black** and the side with the high electron density should appear **yellow**. The colour gradient should then go from **black** to **blue** to **brown-red** to **yellow**. If this can be seen, then it would be possible to make the shift of electrons within a bipolar electrode visible using the conductive polymer polypyrrole.

Several series of experiments have shown that the intercalation of lithium ions has a better colouring effect on the electrochromic recolouring of polypyrrole than sodium ions. For this reason, the following experiment uses lithium perchlorate as the conducting salt rather than sodium sulphate.

2.2. Experiment 2: Using Polypyrrole as a Bipolar Electrode

2.2.1. Equipment and Chemicals

2x platinum electrode, FTO glass with polypyrrole coating, cable, voltage source, plexiglas chamber (internal dimensions 25.0 cm - 1.8 cm - 5.3 cm; source: requests under info@experimente-zur-energiewende.de), lab stand equipment, lithium perchlorate (GHS03 - oxidising; GHS07 - irritant).

2.2.2. Preparation of Electrolyte Solutions

To prepare 100 mL of a 0.1 M LiClO₄ solution, add 1.06 g of lithium perchlorate to a 100 mL volumetric flask. Make up to the mark with distilled water and stir with a magnetic stirrer until the conducting salt is completely dissolved.

2.2.3. Experimental Set-up

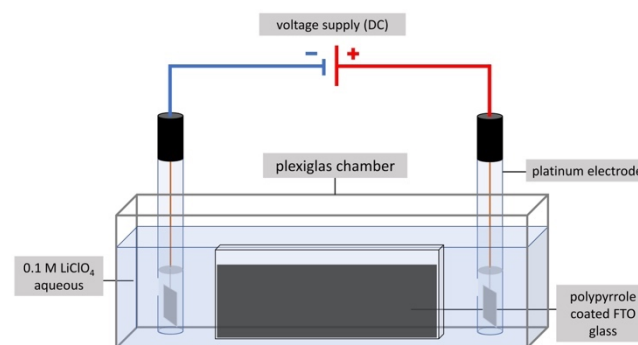


Figure 12. Schematic representation of the experimental set-up for the use of polypyrrole as a bipolar electrode.

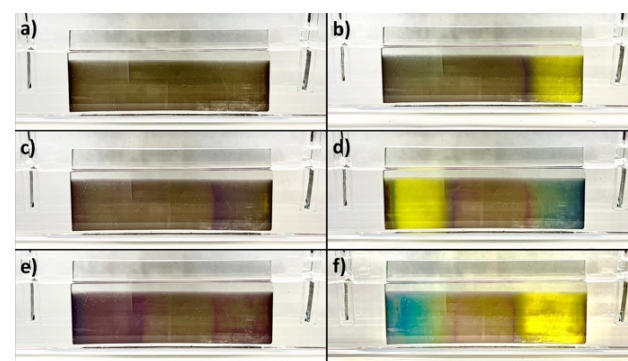


Figure 13. Electrolysis of an aqueous 0.1 M LiClO₄ solution with two platinum electrodes (driving electrodes). A polypyrrole-coated FTO glass disc (as BPE) was placed between the electrodes. a) At the beginning of the electrolysis. b) After about one minute. c) Shortly after interrupting the electrolysis. d) Electrolysis for one minute after reversing the polarity. e) The current supply is interrupted again (about 15 seconds). f) The electrolysis is continued for one minute after the polarity has been reversed for the last time.

2.2.4. Procedure

The experiment is set up as shown in Figure 12. The plexiglas chamber is filled with 100 mL of the 0.1 M lithium perchlorate solution. One platinum electrode is immersed in the electrolyte on the left and the other on the right using a stand and connected to the voltage source by a cable. The coated FTO glass is placed in the electrolyte in the middle between the two platinum electrodes. The distance between the platinum electrodes and the ends of the bipolar electrode should be two centimetres. Electrolysis is then carried out for one minute at a voltage of 10 V. The electrolysis is then stopped and the coated FTO glass is observed for 15 seconds. The polarity is then reversed and electrolysis is repeated for one minute. The electrolysis is stopped again and the BPE is observed for 15 seconds. Finally, the polarity is reversed and the electrolysis is repeated at 10 V for one minute.

2.2.5. Observation

A clear gas evolution can be seen on the platinum electrodes (driving electrodes). After a few seconds, a spreading yellow colouring is visible on the side of

the polypyrrole layer facing the **+ pole** (see Figure 13). On the opposite side, a few small gas bubbles can be seen at the outer edge of the BPE. When the circuit is interrupted, the **yellow** colour disappears and the original colour (**black/brown**) reappears.) Shortly after the first pole reversal, **yellow** staining occurs on the other side of the bipolar electrode (Figure 13, left) and **blue** staining is seen on the other side. Only the leftmost area remains **black** (Figure 13 d). In between you can see the colour changing from **yellow** to **red/brown** to **blue** and finally to **black**. When the current flow is interrupted again, the different colour zones disappear and the colouring is perceived as **brown/black** everywhere. By reversing the polarity again, the four colours can be seen again, but now in reverse order (Figure 13).

2.2.6. Explanation

When a voltage of 10 V is applied to the driving electrodes (platinum) at the **+ pole**, H₂O molecules are oxidised to O₂ and H₃O⁺ ions, and the electrons thus removed travel via the outer circuit to the **- pole**, where water molecules are reduced to H₂ and OH⁻ ions. The reaction equations can be found at the top. As the concentration of the electrolyte has been kept very low (0.1 M), the electrolyte has a high resistance compared to more concentrated solutions. Therefore, the charge difference resulting from the electrolysis of water is not only compensated by the folding mechanism of the H₃O⁺ or OH⁻ ions, but also by the displacement of the electrons inside the bipolar electrode from the side facing the **- pole** to the side facing the **+ pole** (see Figure 14).

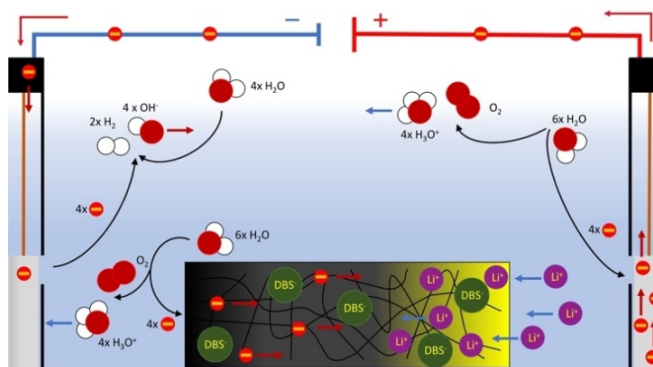


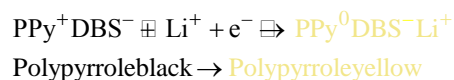
Figure 14. Schematic representation of the processes during the electrolysis of an aqueous 0.1 M LiClO₄ solution at voltages of 10 V. In the centre is an FTO glass coated with polypyrrole.

As the number of electrons on the right side of the BPE now increases (see Figure 14), the polypyrrole is reduced. The negative charge on the right side of the polypyrrole layer increases. The DBS anions incorporated during the electrochemical synthesis are macroanions and are not removed during the reduction due to their size. Therefore, to balance the charge, cations (here: Li⁺ ions) from the electrolyte are deposited into the PPy structure. On the left side of the BPE, no charge balance can take place (except for an adsorption of ClO₄⁻ ions) due to the DBS macroanions by intercalation of perchlorate ions. As the voltage is high enough, water is oxidised to oxygen and H₃O⁺ ions. The electrons migrate through the polymer

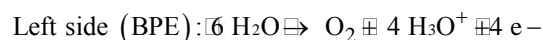
layer to the right of the BPE (Figure 14).

The reaction equations can be written as follows:

Right side (BPE):



Left side (BPE):

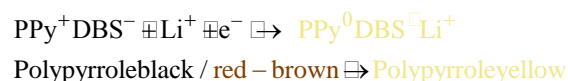


When the electrolysis is interrupted, the electrons are redistributed evenly throughout the polymer. As a result, the Li⁺ ions are removed from the right-hand side. To maintain electrical neutrality, Li⁺ ions are now deposited on the left side. This continues until there is an equal number of Li⁺ ions on both sides (**red/brown**).

As soon as the polarity is reversed, the electrons of the polypyrrole are shifted back to the side facing the **+ pole** (now the left side of the BPE, see Figure 15). Now, Li⁺ ions are again deposited in the polymer to balance the charge (**red-brown** → **yellow**). On the opposite side, there is a shortage of electrons. Li⁺ ions are released to balance the charge (**red-brown** → **blue/black**) (Figure 15).

The reaction equations can be written as follows:

Left side (BPE):



Right-hand side (BPE):

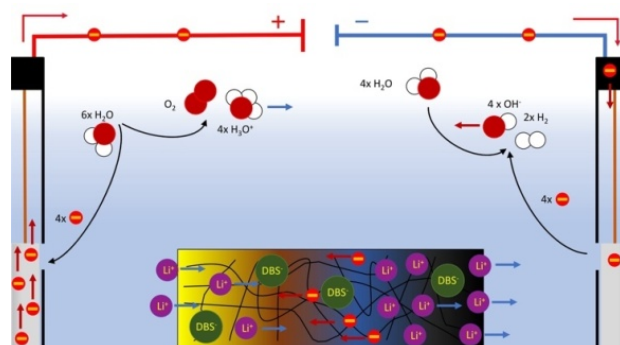


Figure 15. Schematic representation of the electrolysis of an aqueous 0.1 M LiClO₄ solution at voltages of 10 V after one polarity reversal. In the centre is an FTO glass coated with polypyrrole.

When the current is interrupted, the electrons are redistributed evenly throughout the polymer. Li⁺ ions are deposited on the left side and redeposited on the right side until there are equal amounts of lithium ions on both sides. When the poles are reversed, the process is reversed (Figure 16).

The oxygen produced during the first electrolysis can also oxidise the reduced (**yellow**) polypyrrole. This is why

the left side of the polypyrrole layer always appears **black** (Figure 13).

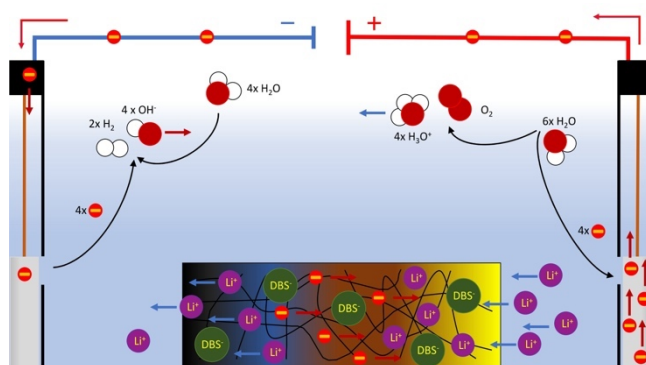


Figure 16. Schematic representation of the processes during the electrolysis of an aqueous 0.1 M LiClO_4 solution at voltages of 10 V after two polarity reversals. In the centre is an FTO glass coated with polypyrrole.

3. Conclusion

With this experiment, the authors have succeeded in visually demonstrating the electron displacement of a bipolar electrode by changing the colour of a polypyrrole layer. This didactic "electron detector" makes it possible to indirectly observe the attraction of electrons by the **+** pole or the repulsion by the **-** pole within a BPE. This experiment underlines the authors' didactically reduced, explanatory approach to the functioning of a bipolar electrode and can also be used in interdisciplinary physics lessons to visualise an E-field.

The authors have designed many more experiments that support the explanation and can also show the fascinating processes of bipolar electrochemistry. Unfortunately, describing all the experiments is beyond the scope of this article, but a few examples should be mentioned.

Among other things, polarisation is very easy to show with a voltage meter. The authors were able to visualise the potential curve within a bipolar electrode by interposing an electric motor. The competition for charge transport between ions and electrical conduction within

the BPE can be shown by concentrating the electrolyte during electrolysis in an open BPE. Many experiments have also been carried out using closed bipolar electrodes (in closed BPE, the charge can only be transported through one bipolar electrode, the driving electrodes are spatially separated from each other).

The authors will report on these experiments in future articles.

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