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ARTICLE TYPE

Achieving Low Voltage Half Electrolysis with a Supercapacitor Electrode

Chuang Peng,[*abc] **Di Hu**[a] **and George Z. Chen**[*a]

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Half electrolysis consists of a single Faradaic reaction and a supercapacitor electrode. The electrolytic product is only produced at the faradaic electrode and the low voltage electrolysis is highly energy efficient.

Studied for over two centuries, electrolysis has many industrial applications, including the extraction and refining of metals, production of various inorganic and organic chemicals, synthesis of nanomaterials, metal anodisation, electroplating, electromachining, and electrokinetic remediation.[1] Electrolysis possesses many advantages, the prime considerations being the simplicity of the electrolytic cell design and the avoidance of the use of an oxidising/reducing agent to drive a redox reaction. However, in today's energy demanding society, the high energy consumption requirement of electrolysis has become a major limitation on the use of this process. Reducing electrolysis voltage is crucial to high energy efficiency and is extensively studied. The use of electrode materials that increase the redox reaction rate is a common route to lowering the activation barrier and hence the voltage of electrolysis. As the most effective example, platinum (Pt) is widely used in fuel cells and many other electrochemical reactions.[2] The limitation of Pt as an electrocatalyst is its high cost and natural scarcity. Another promising approach is photo-electro-catalysis, which utilises the photonic energy with a semiconductor electrode so as to reduce the voltage.[3] However, the stability, kinetics and efficiency of most photocathodes or photoanodes still cannot meet the demand for practical applications.[3,4] Here we show half electrolysis, as a new concept to run a Faradaic redox reaction with the aid of a supercapacitor electrode. In this new process, the unwanted counter electrode reaction is eliminated so the voltage is remarkably reduced, as well as the electrical energy consumption.

Electrolysis involves passing an electric current through the electrolyte to drive a chemical reaction. The electrical energy consumed during electrolysis is determined both by the amount of electric charge and the applied voltage. Since the former is proportional to the electrolytic product obtained at a given current efficiency, a low voltage is highly favoured and in many cases determines the economic justification of electrolysis. In a galvanostatic/constant current electrolysis, the voltage is calculated by

$$U = - E_{rxn} + \eta_A + \eta_C + \Sigma\ IR \qquad (1)$$

where E_{rxn} is the cell potential or overall reaction potential, as determined by the difference between the two half-cell potentials, i.e., $E_{cathodic} - E_{anodic}$, η_A and η_C are the anodic and cathodic overpotentials, and Σ IR is the sum of the ohmic drops across the electrolytic cell.

It is widely accepted that all electrolysis comprises both anodic and cathodic Faradaic charge transfer processes. But in many cases, only one of the electrolytic products is useful, while the other may be unwanted or of little value, or sometimes even hazardous. Therefore part of the electrical energy might be considered as being "wasted" to produce that by-product. Furthermore, a membrane or diaphragm is commonly required to separate the anodic and cathodic products. Electrolysis with only one Faradaic reaction is clearly advantageous to both the energy efficiency and electrolytic cell design. Here we report an electrolysis process with only a single Faradaic half-cell reaction, the other half-cell being provided by a supercapacitor undergoing non-Faradaic double layer charging process. We demonstrate how such a novel approach leads to lower electrolysis voltage and hence reduced electrical energy consumption.

As an emerging technology for energy storage, supercapacitors have been extensively studied in the past two decades and their fast charge/discharge capability and superior cycle performance has been well recognized.[5] High surface area carbons are the state of the art supercapacitor electrode materials. In this study, supercapacitor electrodes are fabricated with Cabot Monarch 1300 pigment black (CMPB), a commercial carbon black with high specific surface area, good conductivity.[6] It exhibits ideal supercapacitor behavior over a wide potential range, with a specific capacitance of 105 F/g (Fig.1A).

The electrolytic cell consists of a titanium (Ti) anode, an aqueous solution containing pyrrole and KCl as the electrolyte, and a cathode of Ti disc modified with or without CMPB [Fig. S1 in the supplementary information (SI)]. The cyclic voltammogram

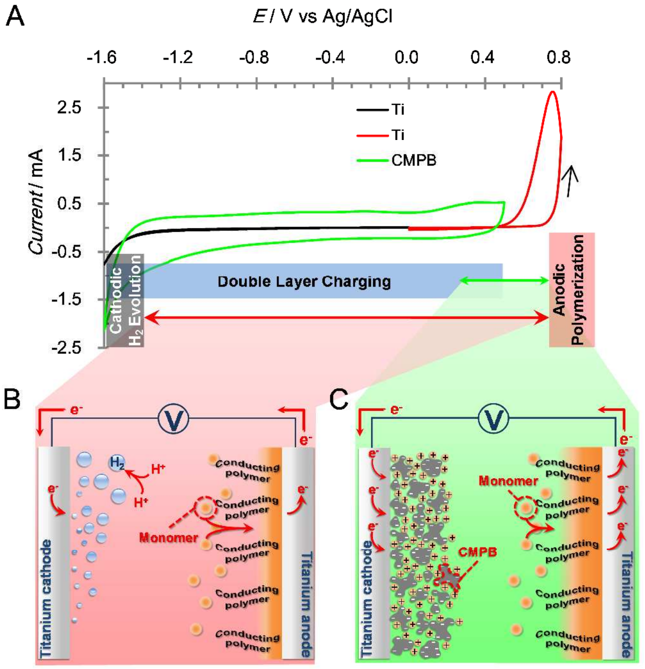

Fig. 1 Electrochemical behaviors of single electrodes and illustrations of the conventional and half electrolysis. (A) Cyclic voltammograms of Ti (0 to 0.8V and 0 to -1.6V) and 0.1 mg CMPB modified Ti (0.5 to -1.6V) in 0.5 M KCl and 0.25 M pyrrole aqueous solution. Potential scan rate: 20 mV/s. (B) and (C), Illustrations of electrolysis in Cell 1 and Cell 2. The red and green double arrows demonstrate the electrolysis voltage of a conventional and half electrolysis, respectively.

(CV) in a three-electrode cell suggests bare Ti is ideally polarised in KCl solution over a wide potential range (Fig. 1A). The onset potential for pyrrole polymerization and hydrogen evolution was 0.68 V and -1.3 V, respectively. Therefore, in a two-electrode cell with bare Ti as both the anode and cathode (denoted as Cell 1, Fig.1B), the anode reaction is the polymerisation of pyrrole and the cathode reaction is the evolution of H_2 (Fig. 1B). The onset potential in CV is equal to the sum of the half-cell potential plus its overpotential and ohmic drop. Therefore, the difference between the two onset potentials is an indication of the minimum voltage that is required to drive the electrolysis in Cell 1, i.e., |-1.3-0.68| = 1.98 V. The CV also shows that the anodic current increases faster than the cathodic current with the overpotential. This suggests the cathodic overpotential constitutes a higher portion of the overall voltage compared to the anodic overpotential during the electrolysis. Therefore, if polypyrrole (PPY) is considered as the desired product of the electrolysis, a high amount of electrical energy is being wasted to produce the by-product, i.e., H_2.

In the electrolytic cell with CMPB modified Ti as the cathode (denoted as Cell 2, Fig. 1C), the electrolysis consists of: (1) a Faradaic anode reaction that is the polymerisation of pyrrole, and (2) a non-Faradaic double layer charging of CMPB as the other electrode process (Fig. 1C). In comparison with conventional electrolytic reactions, the electrolysis in Cell 2 only involves one Faradaic reaction and we use the term “half electrolysis” to classify this type of electrolysis.

To test this theory and the technical advantages of half electrolysis, the two-electrode electrolytic cell was studied by both potentiodynamic (cyclic voltammetric) and galvanostatic electrolysis. As indicated by the notable increase of the CV current in Fig. 2A, the voltage that is required to drive the electrolysis (onset voltage) was 2.0 V for Cell 1 and 0.55 V for Cell 2. The former is in very good agreement with the value calculated from Fig. 1A, i.e., 1.98 V. The latter result, for Cell 2, is remarkably low, suggesting that the initial electrolysis voltage is greatly reduced if the Faradaic cathode is replaced by a double layer supercapacitor.

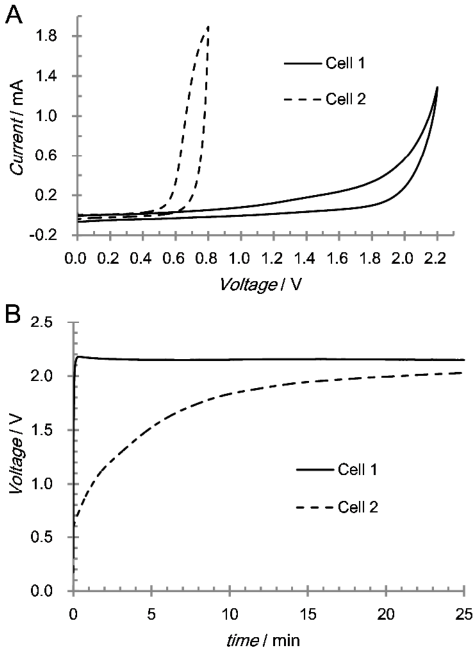

Fig. 2 Comparison between a conventional and half electrolysis. (A) Cyclic voltammograms showing onset voltage of electrolysis in Cell 1 and Cell 2. Voltage scan rate: 20 mV/s. (B) Voltage-time curves of galvanostatic electrolysis in Cell 1 and Cell 2. Cathode of Cell 2: 1.2 mg CMPB modified Ti. Applied DC current: 1.0 mA. Electrolyte: 0.5 M KCl and 0.25 M pyrrole aqueous solution.

In the galvanostatic electrolysis (Fig. 2B), the voltage of Cell 1 reached 2.15 V rapidly and remained almost unchanged. This is slightly higher than the onset voltage of 2.0 V as observed in the CV (Fig. 2A), because of the higher overpotential at the pre-set current value. The voltage of the half electrolysis is determined by

$$U = |OCP^{o} - E_{anodic}| + \eta_{A} + It/C + \Sigma\, IR \qquad (2)$$

Here OCP° is the initial open circuit potential of the supercapacitor electrode, C is the capacitance, and I is the applied current. The front part of the equation, $|OCP^{o} - E_{anodic}|$, is similar to the cell potential, E_{rxn} of a conventional electrolysis. It is also an indication of the minimum required voltage in half electrolysis. The initial voltage of the galvanostatic half electrolysis was 0.586 V (Fig. 2B). Prior to the electrolysis, the OCP of the CMPB modified Ti cathode was measured as 0.327 V (Fig. S2 in the SI). Therefore, the difference between the anodic half-cell potential and the initial OCP of the CMPB supercapacitor electrode, i.e., $|OCP^{o} - E_{anodic}|$ is calculated as 0.68 - 0.327 = 0.353 V. This explains the origin of the substantial difference in the initial electrolysis voltage of Cell 1 and Cell 2, as illustrated by the green and red double-arrow lines in Fig. 1A.

As the half electrolysis proceeds, the voltage increases because the potential of the CMPB electrode has shifted to more negative values. This fact is also demonstrated by Equation 2, that the value of It/C increases as electrolysis proceeds. While the potential of the CMPB electrode reaches and exceeds the H^+/H_2 half-cell potential, the cathodic process will eventually become the evolution of H_2.

The low voltage of half electrolysis stems from the absence of one Faradaic reaction. As indicated earlier, the overpotential of hydrogen evolution on Ti electrode is very high in Cell 1, resulting in a high electrolysis voltage. However, the high overpotential for hydrogen evolution was averted in Cell 2. Therefore, the half electrolysis is expected to be highly energy efficient. The electrical energy consumed during galvanostatic electrolysis is calculated by

$$W = \int IUdt \qquad (3)$$

where the measured voltage U is a function of time t and I is the applied current. As summarised in Table 1, the electrical energy consumption of Cell 2 was lower than that of Cell 1 over any time period, especially at the initial stage where the voltage of Cell 2 was low. Since the same current passed through both cells, the total electric charges of the two electrolytic reactions were the same during the same time period. Therefore, to produce the same amount of PPY, much less electrical energy was consumed in the half electrolysis.

Table 1 also shows that a higher amount of energy could be saved when the duration of electrolysis is shorter or the total amount of electric charge is smaller. Analogously, if the capacitance value of the CMPB electrode is higher, the half electrolysis would be more energy efficient. This trend is also indicated by Equation 2 that the voltage increases slower if a higher-capacitance electrode is used. When less CMPB (0.2 mg) was used, the electrolysis voltage reached a constant value of 2.09 V in less than 3 minutes (Fig. 3). While for 1.2 mg CMPB, the electrolysis voltage increased to 2.03 V after 25 minutes of electrolysis. For the same time period of electrolysis, less energy is consumed by increasing the capacitance value of the CMPB supercapacitor electrode (Table 1 and Table S1).

After 25 minutes of half electrolysis in Cell 2 (Fig. 2B), the Ti anode was covered by a thin and uniform PPY film (Fig. S1B). The SEM images (Fig. S4A and B) suggested the same morphology for PPY prepared by half and conventional electrolysis. The surface of both PPY films was characterized by numerous nodules with approximate diameter of 2 µm. The two PPY films also exhibited the same electrochemical behaviour (Fig. S4C) and rectangular CV shapes, typical of a supercapacitor electrode. The capacitance is calculated as 113.5 and 106.4 mF for PPY prepared and half and conventional electrolysis. The similar CV currents and capacitance values indicate the amount of PPY prepared by the two electrolysis processes are very similar, i.e. equal current efficiency.

As the half electrolysis proceeds to some extent, the electrolysis voltage of Cell 2 becomes very close to that of Cell 1. To reuse the CMPB supercapacitor electrode, its electrode potential has to be restored to a more positive value. Although the exact mechanism is not clear, supercapacitors are well known for their fast self-discharge or potential decay.[8] This is a clear disadvantage in energy storage. However, the fast self-discharge turns to a merit in the half electrolysis application. Experiment showed that the OCP of the CMPB electrode increased from -0.57 to 0.02 V in less than two hours (Fig. S5). After the OCP was recovered, the CMPB was reused in the half electrolysis and the resulting voltage-time curve was very similar to that of the electrolysis with a freshly prepared CMPB electrode (Fig. S6). This suggests the possibility of designing a continuous process for half electrolysis with a moving supercapacitor electrode, such as rotating or conveyor belt electrode. In such an electrolytic cell (Fig. S7), only part of the supercapacitor electrode is immersed in the electrolyte solution and used in the half electrolysis while the remaining part is allowed to undergo potential relaxation/self-discharge. As a result, the electrolysis voltage would remain at a constant low value. If combined with other processes, it is also possible that the energy stored in the supercapacitor electrode can be utilized to further improve the energy efficiency. The mass specific capacitance of electrodes with faradaic pseudocapacitance is generally higher than double layer supercapacitors. In Fig. S8, we have demonstrated that half electrolysis can also be achieved by using an electrode with pseudocapacitance.

Copper electrowinning is an industrial electrolysis process to produce copper metal at the cathode, along with oxygen evolution at the anode. A high anodic overpotential is required to drive the oxygen evolution reaction at a fast rate.[9] Therefore, a large part of the electric energy is consumed to produce this by-product. A conventional approach to improving the energy efficiency is the selection of anode materials to lower the overpotential of oxygen evolution.[9] As shown in Fig. 3, the electrolysis voltage was 1.4 V with a commonly used lead anode. If the lead anode is replaced with a supercapacitor electrode, the voltage was 0.42 V initially and gradually increased as the electrolysis proceeded. To the best of our knowledge, this initial electrolysis voltage is the lowest reported value for any copper electrowinning process. This notable difference in electrolysis voltage is because the oxygen evolution reaction is eliminated in the half electrolysis. The energy consumption of industrial copper electrowinning is

Table 1. Summary of the electrical energy consumption (W) of Cell 1 and Cell 2 during different time periods of galvanostatic electrolysis. Calculated from Fig.2B.

Time duration / min	0-0.5	0.5-1	1-5	5-10	10-15	15-20	20-25	0-25
$W_{Cell\ 1}$ (mJ)	62.3	65.2	518.0	645.0	646.3	646.8	645.7	3227.9
$W_{Cell\ 2}$ (mJ)	20.8	26.0	305.9	511.7	568.7	591.7	604.0	2628.1
$W_{Cell\ 2}/W_{Cell\ 1}$ ×100%	33.3%	39.9%	59.1%	79.3%	88.0%	91.5%	93.5%	81.4%

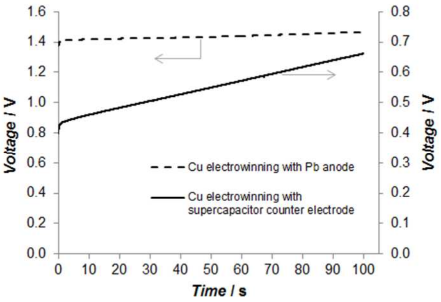

Fig. 3 Half electrolysis in copper electrowinning. Voltage-time curves of galvanostatic electrolysis of H_2SO_4 and $CuSO_4$ aqueous solution. Current: 2 mA. Anode: Pb disc or 5 mg CMPB modified Pb disc.

measured as kWh of electricity per kg of copper (kWh/kg Cu). Under our experimental conditions, the theoretical energy consumption at 100% efficiency is calculated as 0.761 kWh/kg Cu with oxygen evolution as the anodic process (SI). In Fig. 3, the energy consumption of the conventional and half electrolysis is calculated as 1.265 and 0.485 kWh per kg Cu (SI). The half electrolysis only used 38% of the electric energy compared with the conventional electrolysis with a lead anode. Moreover, the energy consumption of half electrolysis was also lower than the thermodynamic minimum energy requirement in conventional Cu electrowinning.

So far, we have reported half electrolysis, a new electrolytic process with a single Faradaic charge transfer electrode and a supercapacitor electrode. The product of half electrolysis is only generated in the vicinity of the Faradaic electrode, so a separator can be avoided in the cell design. Furthermore, the initial voltage and electrical energy consumption of half electrolysis is considerably low compared to conventional electrolysis. The process benefits from a higher capacitance electrode or a shorter duration electrolysis to achieve high energy efficiency. The electrolysis voltage increases as electrical charge gradually builds up on the supercapacitor electrode. However, our results suggest a steady low electrolysis voltage can also be accomplished by using a moving-electrode supercapacitor. We anticipate this paper to be a starting point for a wide spectrum of applications of half electrolysis, to achieve simplicity of cell design and low energy consumption.

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Notes and references

[a] *Department of Chemical and Environmental Engineering, and Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham, UK NG7 2RD. Tel: +44 0115 951 4171; Email: george.chen@nottingham.ac.uk*
[b] *College of Engineering, Mathematics and Physical Sciences, University of Exeter, Cornwall Campus, Penryn, Cornwall, UK*
[c] *Present address: Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo Campus, Ningbo, Zhejiang, China 315100. Tel: +86 (0)574 8818 9340; E-mail: Chuang.peng@nottingham.edu.cn*

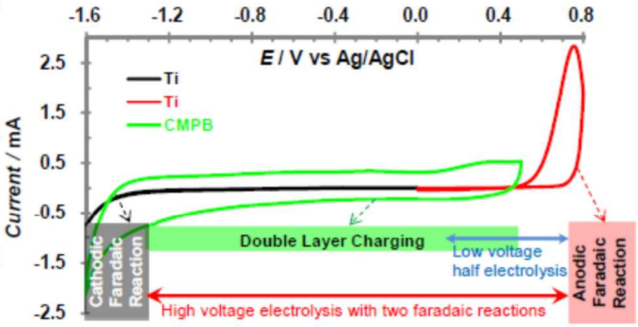
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1 (a) J. Thonstad, Aluminium Electrolysis: Fundamentals of the Hall-Heroult Process, (Aluminium-Verlag: Dusseldorf, ed. 3, 2001); (b) T.K. Rose, *Nature* 1915, **95**, 100; (c) K. Haradak, S. Suzuki, *Nature*, 1977, **266**, 275; (d) M. P. Zach, K. H. Ng, R. M. Penner, *Science*, 2000, **290**, 2120; (e) H. Masuda, K. Fukuda, *Science*, 1995, **268**, 1466; (f) R. Schuster, V. Kirchner, P. Allongue, G. Ertl, *Science*, 2000, **289**, 98; (g) Y. B. Acar, A. N. Alshawabkeh, *Environ. Sci. Technol.*, 1993, **27**, 2638.
2 (a) V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, N. M. Marković, *Science*, 2007, **315**, 493; (b) N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, *Science*, 2007, **316**, 732; (c) B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu, Y. Xia, *Science*, 2009, **324**, 1302.
3 (a) A. J. Bard, M. A. Fox, *Acc. Chem. Res.*, 1995, **28**, 141; (b) M. Tomkiewicz, J. M. Woodall, *Science*, 1977, **196**, 990; (c) O. Khaselev, J. A. Turner, *Science*, 1998, **280**, 425.
4 (a) S. Ida, K. Yamada, T. Matsunaga, H. Hagiwara, Y. Matsumoto, T. Ishihara, *J. Am. Chem. Soc.*, 2010, **132**, 17343; (b) R. E. Blankenship, *Science*, 2011, **332**, 805.
5 (a) B. E. Conway, *J. Electrochem. Soc.*, 1991, **138**, 1539; (b) A. S. Arico, P. Bruce, B. Scrosati, J. Tarascon, W. van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366; (c) R. F. Service, *Science*, 2006, **313**, 902; (d) P. Simon, Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845; (e) J. Chmiola, C. Largeot, P. L. Taberna, P. Simon, Y. Gogotsi, *Science*, 2010, **328**, 480.
6 C. Peng, S. W. Zhang, X. H. Zhou, G. Z. Chen, *Energy Environ. Sci.*, 2010, **3**, 1499.
7 C. Peng, J. Jin, G. Z. Chen, *Electrochim. Acta*, 2007, **53**, 525.
8 (a) J. J. Niu, B. E. Conway, W. G. Pell, *J. Power Sources*, 2004, **135**, 332; (b) M. Kaus, J. Kowal, D. U. Sauer, *Electrochim. Acta*, 2010, **55**, 7516; (c) Q. Zhang, J. Rong, D. Ma, B. Wei, *Energy Environ. Sci.*, 2011, **4**, 2152.
9 (a) I. Ivanov, Y. Stefanov, Z. Noncheva, M. Petrova, T. Dobrev, L. Mirkova, R. Vermeersch, J. P. Demaerel, *Hydrometallurgy*, 2000, **57**, 125; (b) M. Clancy, C. J. Bettles, A. Stuart, N. Birbilis, *Hydrometallurgy*, 2013, **131–132**, 144.

Broader Context

Electrolysis is an important method in mineral processing, manufacturing and environmental technologies. A low electrolysis voltage is key to high energy efficiency. This paper demonstrates a supercapacitor electrode, often used for energy storage, can be combined with a faradaic electrode to achieve electrolysis at low voltage. This new process, i.e. half electrolysis involves only one faradaic reaction, differing from conventional electrolysis which requires two faradaic reactions, both consuming electric energy. The unique feature of half electrolysis is its single faradaic reaction, leading to advantages of low energy consumption and simplicity of cell design. This new concept is verified by two examples, in which a supercapacitor electrode replaces either the faradaic anode or cathode. Both examples exhibit significantly lower voltage and energy consumption compared to conventional electrolysis. Improving energy efficiency is very important to tackling energy shortages and reducing carbon emission. It is our hope that half electrolysis will contribute to the energy efficiency of various industrial processes.

TOC graphic



TOC text

Half electrolysis consists of one Faradaic reaction and a supercapacitor double layer charging process. In such a configuration, the product of the electrolysis is only generated in the vicinity of one electrode. Furthermore the electrolysis voltage and electric energy consumption is significantly reduced.