Cambridge Reactor Design
Unit D2
Brookfield Business Centre
Twentypence Road, Cottenham
Cambridge, CB24 8PS

T +44 (0) 1954 252522
F +44 (0) 1954 252566
E sales@crduk.com
W www.crduk.com

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Cambridge Reactor Design

AMMONITE SPIRAL ELECTROCHEMICAL CELLS

USER GUIDE

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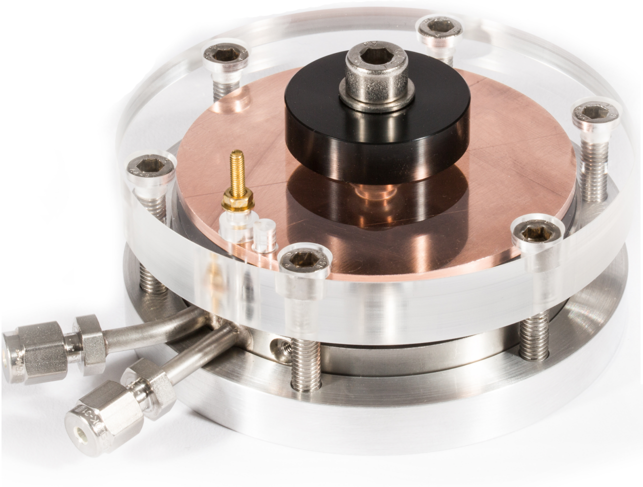
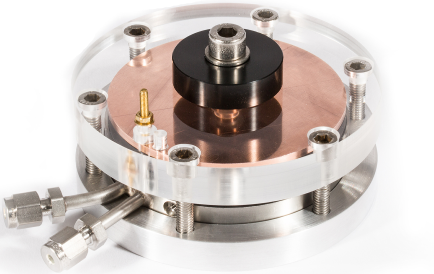
Authors: Dr R. A. Green, Prof R. C. D. Brown and Prof D. Pletcher – University of Southampton



Ammonite15



Ammonite8

AMMONITE

SPIRAL ELECTROCHEMICAL FLOW CELL

Contents

1. Shipping and Unpacking. Important Notice.

The Electrochemical Cell is foam packed in a purpose made box.

Unpack the equipment carefully, lifting out vertically and check for any damage – any damage sustained during transport must be reported immediately to the courier.

The box should be stored as it may be useful if the Electrochemical needs to be returned, serviced or upgraded.

2. Warranty

The warranty period is 12 months. For claims under the warranty, contact your local dealer. You may need to send the machine to our works giving reasons for the claim. You will be liable for freight costs.

The warranty does not cover worn out parts, nor does it apply to faults arising from improper use, insufficient care or maintenance not carried out in accordance with the instructions in this operating manual.

3. Introduction

The Ammonite family of electrolysis cells are microflow cells designed for convenient electrosynthesis in the environment of an organic synthesis laboratory. The cells are designed to permit:

- A selective chemical conversion by electrolysis.
- A high conversion during a single pass of the reactant solution through the cell.
- The formation of multigrams of product at a high conversion rate (multigrams/hour).
- A short residence time of the reactant/product within the reactor.

These characteristics are very unusual with electrolysis cells. Typically, electrolyses in the literature are carried out in:

a. Beaker cells with reactions commonly terminated with a low conversion after many hours.

b. Flow cells that recycle the solution from a reservoir. A low conversion from each cycle of the reactant solution through the cell is achieved. The residence time of reactant/products in the cell and reservoir is again typically hours.

The performances of the Ammonite 8 and Ammonite 15 reactors are achieved by combining a long microflow channel with efficient mass transport. The electrodes are circular and the electrolyte microflow channel is spiral. The key dimensions in the cell are shown in table 1.

Cell	**Electrode diameter cm**	**Microflow channel length, L cm**	**Microflow channel width, w cm**	**Interelectrode gap, y cm**	**Typical product formation rate g/hour**
Ammonite8	8.5	100	0.2	0.05	0.1 - 5
Ammonite15	14.8	200	0.5	0.05	1 - 20

Table 1 - *Key dimensions of the Ammonite 8 and Ammonite 15 Laboratory Electrolysis Cells.*

In addition to the Ammonite cell, an electrosynthesis will require pumps capable of delivering the required flow rate and a constant current power supply. Many laboratories will already have suitable pumps and power supplies. If not, top of the range equipment is probably unnecessary.

4. Ammonite Reactor Components

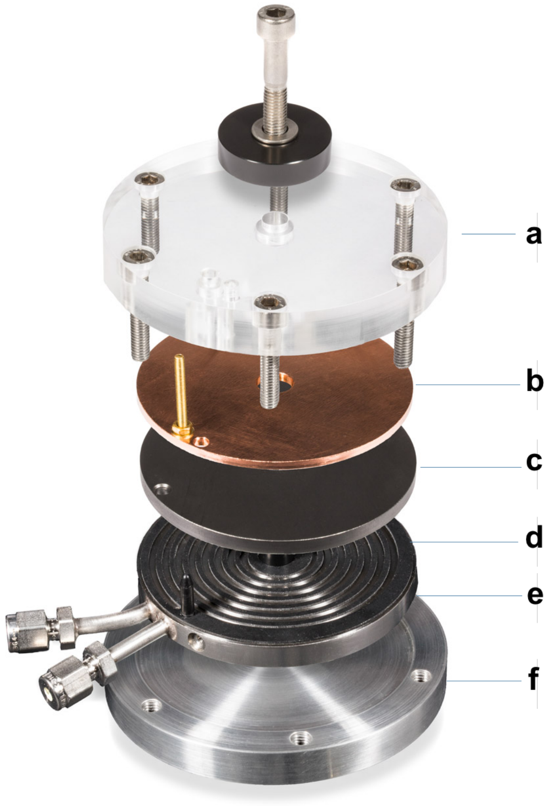


Figure 1 - *Components of the Ammonite 8 Reactor.*

a)	Perspex top plate with bolts
b)	Copper plate electrical contact
c)	Carbon/PVDF working electrode
d)	Base plate (Insulating spacer not shown)
e)	Gasket
f)	Stainless steel counter electrode with recessed channel

5. Safety

For your protection

The safety of the operator cannot be guaranteed if the equipment is used contrary to the safety statements and operating procedures described in this manual, or used outside the manufacturer's specifications, or if it has been modified by a 3rd partyTo ensure safe use of the Ammonite Spiral Electrochemical Cells the advice in this user guide must be followed:

- Follow the safety instructions
- Read the user manual in full before starting up this equipment
- Keep the user manual in a place where it can be accessed by everyone
- Set up the equipment on a level, stable, non-slip, fireproof surface
- Check the appliance and accessories for damage before each use. Do not use damaged components
- Be aware that the unit may heat up when in use
- Wear PPE according to the hazard category of the media being processed.
- Beware hazards due to
  - combustible media with low boiling point
  - flammable materials
- Do not operate the equipment in an explosive atmosphere
- Safe operation is only guaranteed with accessories supplied or recommended by Cambridge Reactor Design
- Always turn off the equipment and disconnect from the mains electricity supply before attaching accessories
- The equipment must only be opened by trained experts
- Electric charge is being used to drive chemical transformation. Contact with metal components should be avoided while the cell is in operation, particularly when high cell currents are being used.
- Hydrogen generation is a common counter electrode reaction (see section 5.4 gas evolution) that can be formed in the Ammonite cells. **Hydrogen gas is extremely flammable, and Hydrogen gas/air mixtures can be explosive.** Ensure the Ammonite reactor is used in a well ventilated fumehood, away

from any source of ignition. The amount of hydrogen gas that can be formed is proportional to the current used (see section 5.4 gas evolution), therefore extra caution needs to be observed when operating the Ammonite cells at higher currents.

- While the material of construction have been chosen for their stability to many reagents, solvents, etc., consideration should be given to their stability when using new conditions.

Correct Use

Use

- For Flow Electrochemistry applications

Range of Uses

- Laboratories
- Universities
- Schools

The safety of the user cannot be guarantied if the appliance is operated with accessories that are not supplied or recommended by the manufacturer or if the appliance is operated improperly contrary to the correct use and the manufacturers specifications or if the appliance is modified by a 3rd Party.

6. Understanding the Ammonite Cell

Symbol	Typical Units	Definition
c_x	mole cm^{-3}	Concentration of reactant at distance x along the channel.
c_{in}	mole cm^{-3}	Concentration of reactant at channel inlet.
c_{out}	mole cm^{-3}	Concentration of reactant at channel outlet.
F	C $mole^{-1}$	The Faraday constant.
f	$cm^3\ s^{-1}$	Volumetric flow rate of reactant solution.
I_{cell}	A	Experimental cell current
$I_{cell.m.t}$	A	Cell current when reaction mass transfer controlled.
$I_{cell,minimum}$	A	Minimum cell current to achieve full conversion
$k_{m,x}$	cm s^{-1}	Mass transfer coefficient.
L	cm	Length of microflow channel.
m	-	Number of moles of reactant.
n	-	Number of electrons/reactant molecule involved in electrode reaction.
t	s	Length of electrolysis/reaction
V_{soln}	cm^3	Volume of reactant solution.
$V_{channel}$	cm^3	Volume of microflow channel. = xyL
w	cm	Width of microflow channel.
X	-	Fractional conversion of reactant to product.
x	cm	Distance along channel from solution inlet.
y	cm	Interelectrode gap.
φ	-	Fraction of full charge passed used for desired reaction.

Table 2 - *Definition of symbols.*

During electrolysis, chemical change is dependent on the passage of charge through a complete cycle comprising the electrodes, the electrolyte and the external circuit. Across the working electrode surface, the electrons are transferred via an electron transfer reaction, eg.

$$\mathrm{R} - ne^{-} \longrightarrow \mathrm{P} \qquad (1)$$

The rate of chemical change is the current density (current per unit area) and this depends on the potential of the electrode.[1] The fastest chemical change occurs when the reaction is 'mass transfer controlled', ie. once the reactant, R, reaches the working electrode surface the conversion of R to P occurs immediately.

Most electrolysis cells are designed so that the chemistry and its rate are uniform over the entire electrode surface. This requires that the current density and hence the concentration of reactant are uniform over all the surface of the electrode. This is not the case with the Ammonite Cells, see figure 1. A key objective is a high conversion in a single pass of reactant solution through the cell and to meet this goal, the concentration of the reactant must drop from the initial value at the cell inlet towards zero as the solution passes along the microflow channel; the local current density will follow the drop in reactant concentration (see figure 3)

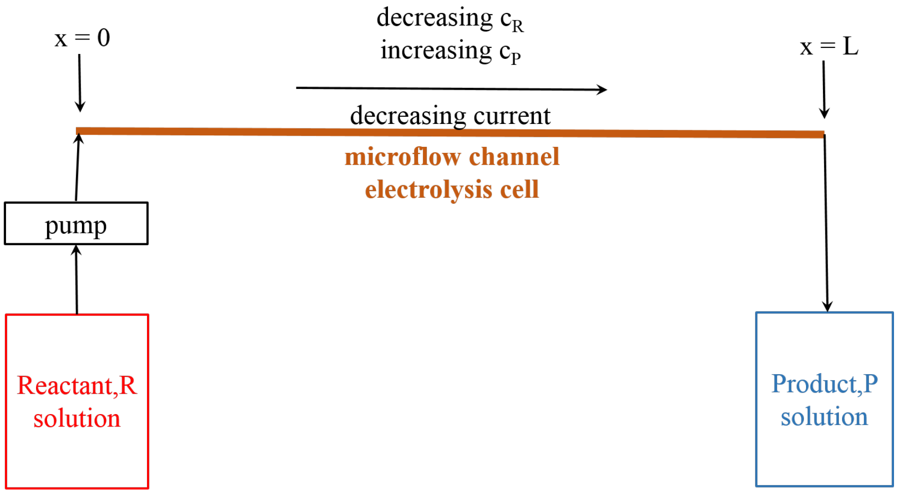
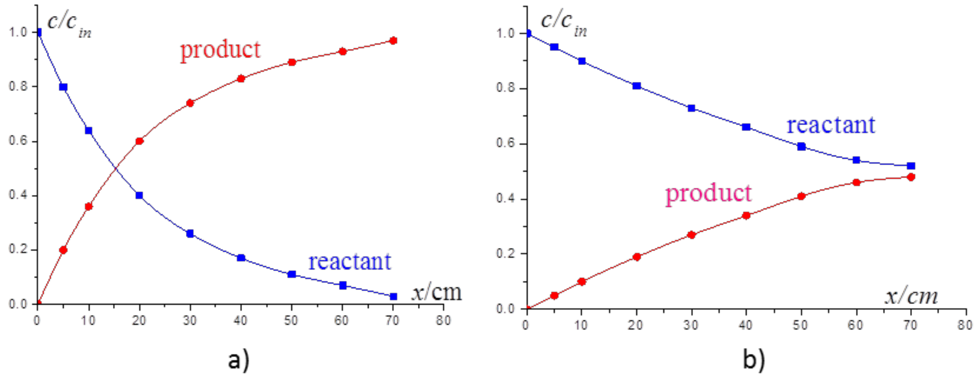


Figure 2 – *Schematic of the Operation of the Ammonite Cell.*

In fact, the concentration of reactant and hence the local current density (proportional to the local reactant concentration) will drop approximately exponentially along the channel,[2] reaching close to zero with appropriate electrolysis conditions (particularly the cell current), see figure 3.



a) b)

Figure 3 - *Model calculations of the concentrations of reactant and product as a function of distance along the channel, x. (a) ideal volumetric flow rate (b) too high flow rate to achieve full conversion. The cell current will follow the reactant concentration.*

6.1 Selection of Cell Current

Only the total cell current can be controlled/measured with the Ammonite Cells. The correct selection of the cell current for the concentration of reactant and the flow rate of the reactant solution through the cell is critical to the selectivity of the synthesis and the rate of conversion. Full conversion of reactant to product both maximises the product yield and simplifies the isolation of pure product.

Full conversion in a single pass in an electrolysis is dependent on passing a large enough charge through the cell to satisfy mass balance in the synthesis reaction (considered as an oxidation)

$$\mathrm{R} - ne^{-} \longrightarrow \mathrm{P} \qquad (1)$$

while the reactant is in the microflow cell. The cell current is calculated using Faraday's law; assuming no competing electrode reactions, the charge for full conversion is mnF where m is the number of moles of reactant, n the number of electrons involved in the synthesis reaction and F (C mole^{-1}) the Faraday constant (the charge on a mole of electrons). Therefore, the minimum cell current (in amps) for full conversion is given by

$$I_{cell,minimum} = mnF/t \qquad (2)$$

where t (s) is the time to pass the reactant solution containing m moles of reactant through the cell. This time is, of course, determined by the flow rate of the reactant solution. If the cell current is below this value, full conversion cannot be achieved and if it is above, then a competing reaction must be occurring at the working electrode; the product is being degraded by overoxidation or solvent/electrolyte is being oxidised, possibly leading to unwanted material in the outlet stream.

It is clear from equation (2) that the required cell current will increase proportional to the concentration of reactant in the inlet solution and the flow rate of the reactant solution through the microflow channel. In the limit, if too high values are selected for the reactant concentration and/or flow rate, the required cell current may be unachievable (see next section) or lead to other problems such as Joule heating of the solution (see section 5.5).

It is important to recognise that it is inherent in any electrolysis designed to give full conversion that the current distribution over the working electrode surface is very non-uniform. The current density must be high close to the inlet where the reactant concentration is high and drop towards zero at the outlet when the reactant has been converted to product. The simplest model for the cells shows that the local current and the reactant concentration both decay exponentially with distance along the electrode, see figure 3.[3]

6.2 What Limits the Useful Cell Current

In addition, clean synthesis requires that the desired electrode reaction is the predominant, and preferably, the only chemical change at the electrode at all points along the microflow electrolysis channel. This is only possible if the desired chemical change is fast enough. The maximum rate at which chemical change occurs at a surface is always limited by the rate at which the reactant reaches the surface. Hence the fastest chemical change occurs when the synthesis reaction is mass transfer limited at all points on the working electrode. In electrolyses in the extended channel microflow cell, the overall rate of chemical change is proportional to the cell current and the cell current is the sum of all the currents along the channel. If the synthesis reaction is mass transfer controlled, the cell current, $I_{cell,mt}$ (amps), is given by

$$I_{cell,mt} \; = \; \int_0^L I_{x,mt}\, dx = nFw \; \int_0^L k_{m.x}\, c_x\, dx \qquad (3)$$

where x (cm) is the distance along the channel, $I_{x,mt}$ (amps) the mass transport limited current at the distance x along the channel and L the total length of the channel, w (cm) is the width of the microflow channel, $k_{m,x}$ (cm s^{-1}) the mass transfer coefficient at the distance x along the channel and c_x (mol cm^{-3}) the concentration of reactant at this distance. The mass transfer coefficient characterises the mass transfer regime in the microflow channel and in the simplest situation is only determined by the dimensions of the channel and the flow rate. In reality, however, it can be influenced by corners in the flow path and by gas evolution at either electrode (gas bubbles act as turbulence promoters while the volume of gas increases the linear flow rate of the reactant solution through the cell). Then, the mass transfer coefficient becomes a function of distance along the channel. Although the mass transfer coefficient (and hence the cell current) increases with the flow rate, the relationship is less than first order and therefore the highest conversions are obtained at low flow rates. Certainly, it is clear that efficient mass transport (high k_m) is advantageous in seeking a high conversion and product formation rate. Provided the conversion can be maintained, a high flow rate is advantageous in achieving a high rate of product formation.

6.3 Fractional Conversion

To achieve full conversion using the cell current, $I_{cell,minimum}$, the synthetic reaction must be occurring without competing reactions and this is only possible if the mass transport controlled cell current is large enough that only the synthesis reaction is occurring at the working electrode, ie. $I_{cell,mt}$ must be greater than $I_{cell,minimum}$.

For a mass transfer controlled reaction, the actual fractional conversion, X, for any solution flow rate, f (cm^3 s^{-1}), can be estimated from the equation [3]

$$X = 1 - {}^{c_{out}}/_{c_{in}} = 1 - \exp^{-k_m wL}/_{f} \qquad (4)$$

where w (cm) is the width of the channel, L (cm) the length of the channel and k_m (cm s^{-1}) the length averaged mass transfer coefficient. In the absence of gas bubbles, the mass transfer coefficient as a function of flow rate can be determined and while this value is an underestimate for most synthesis conditions, it can be used to give an initial estimate of cell performance.[4] If the reaction is not mass transfer controlled, the fractional conversion will be less.

To summarise, full conversion of reactant to product is only possible if:

- The cell current is high enough that the charge demanded by Faraday's law (mass balance) is passed while the reactant remains in the microflow cell, ie.

$$I_{cell} \geq I_{cell,minimum}$$

- The synthesis reaction is fast, ideally mass transfer controlled and the mass transfer conditions are good enough that the mass transfer controlled cell current for the synthesis reaction exceeds this current ie.

$$I_{cell} \leq I_{cell,mt}$$

- The length of the microflow channel is sufficient at the flow rate used.

6.4 Rate of Product Formation

In ideal conditions where there is only the synthesis reaction occurring at the working electrode and full conversion can be achieved, the rate of product formation is given by

$$Rate = m/t \tag{5}$$

In most situations, the fractional conversion, X, is less than one and reactions of intermediates in the synthesis reaction lead to some byproduct so that the fractional selectivity, ϕ, is also less than one, when the rate of product formation will be less and given by

$$Rate = \phi X m/t \tag{6}$$

ϕX is the chemical yield of product which can be used directly. The rate of formation of the product may be increased by increasing the reactant concentration in the feed or the flow rate of the reactant but either will require an increased cell current and maintaining the synthesis reaction as the sole/dominant reaction at the working electrode.

7. Practical Advice

7.1 Cell Current

In most cases, with a new electrosynthesis, several of the quantities in the discussion (eg. the mass transfer coefficient, the reaction selectivity and possible fractional conversion) will not be known. The above discussion is therefore intended to provide an understanding of the concepts of extended channel length microfluidic cells essential to optimum use of the cells. In practice, the performance of the cells must be determined experimentally but it is strongly recommended that the initial experiments use a cell current slightly above the value of $I_{cell,minimum}$ calculated from equation (2).

7.2 Electrolyte Addition

Because of the narrow interelectrode gap in the Ammonite Cells, electrosyntheses are possible with only a low concentration of electrolyte. Together with the high conversion of R to P, a low concentration of electrolyte can greatly simplify the recovery of pure product from the cell outlet solution. But the addition of some electrolyte is usually advantageous. Typically, in a beaker cell, the concentration of electrolyte is 1 M while in an Ammonite Cell it can be as low as 1 – 10 mM. The use of a low electrolyte concentration can also increase the range of possible electrolytes and therefore, for example, avoid the use of expensive tetraalkylammonium salts in organic solvents. When the reactant is charged, no electrolyte addition is necessary.

7.3 Electrolysis Time

In order to prepare a few grams of products or less in an Ammonite Cell, the electrolysis will be completed in a few minutes (electrolysis time = volume of reactant solution/flow rate). With electrolysis in beaker or macroflow cells, the time spent by reactant and product in the system is usually many hours and this gives rise to the possibility for degradation of performance due to slow homogeneous reactions, eg. hydrolysis.

The residence time (volume of cell channel/flow rate) of the reactant/product in the Ammonite cell is generally less than 1 minute and can be as short as ~ 10 s. The outlet solution can be passed to another reactor, composition adjusted, cooled etc and this further reduces the importance of side reactions.

7.4 Gas Evolution

Hydrogen evolution is often a convenient counter electrode reaction. Originally, there was a concern that the gas formed would block the microflow channel and prevent further electrolysis. Experience shows that this is not the case and, indeed, the performance found when H_2 is evolved is usually superior to that predicted by the simple theory.[3] This can be understood in terms of an enhanced mass transfer coefficient resulting from turbulence around small gas bubbles and the gas volume formed increasing the linear flow rate of solution through the cell. The enhanced mass transfer regime will lead to an improved selectivity through a higher mass transfer controlled cell current for the synthesis reaction, $I_{cell,mt}$ (see equation (3)) as well as an improved conversion (see equation (4)).

Caution: If the counter electrode reaction is H_2 evolution, the cell should be operated in a well ventilated area. The Ammonite 15 cell has been used with a cell current of 12 A, where the rate of H_2 evolution is > 80 cm^3 min^{-1}.

7.5 High Currents

The rate of product formation can be increased by increasing either the concentration of reactant or the flow rate of the solution through the cell. Both strategies necessitate an increase in cell current in order to achieve a high conversion. One consequence is an increase in the volume of H_2 gas formed and at higher cell currents this can be significant (**see caution above**). For example, a cell current of 1.0 A will lead to the evolution of ~ 7 cm^3 min^{-1} of gas, comparable to the flow rate of reactant solution and therefore leading to a significant increase in the flow rate.

A second consequence is Joule heating of reactant solution as it passes through the cell. The increase in temperature depends on the cell current and the residence time of the reactant solution in the cell. When the inlet solution is at a temperature of 298 K, heating is generally not significant for cell currents < 1 A. For larger cell currents there can be a temperature increase large enough to increase the mass transfer coefficient (advantageous) but also to cause concern about a degredation of reaction selectivity. Temperature rise becomes more of an issue for electrolyses with a low/no electrolyte in organic solvents or where a cooled inlet solution is desirable. Then cooling of the cell is essential and the use of a **Polar Bear** (Cambridge Reactor Design) should be considered.

7.6 Materials Stability

The materials for components in the Ammonite Microflow Electrolysis Cells have been chosen with stability in mind. The stainless steel cathode is suitable for H_2 evolution and stable to corrosion in many media. The C filled PVDF (polyvinylidene fluoride) anode is a robust anode material. The spacer is manufactured from

KALREZ (FFKM), a polymer stable to many organic solvents/reactants, aqueous acids and alkalis. But Cambridge Reactor Design cannot guarantee the stability of components in all media and conditions. ***Caution: Consider and test stability of cell components in new media and reaction conditions.***

8. Planning a Procedure

Good performance in an Ammonite Cell is dependent on controlling both the chemistry occurring in the cell and the electrolysis conditions.

8.1 The Working Electrode Reaction

Electrode reactions involve the transfer of electrons between the reactant and the working electrode. Usually, the transfer occurs in single electron steps and the initial electron transfer generally leads to an intermediate with radical characteristics (O). The conversion of reactant to stable product usually requires the transfer of at least two electrons (leading to bond cleavage and/or bond formation).

$$\mathrm{R} - e^{-} \longrightarrow \mathrm{O} \xrightarrow{\text{chemistry, - } e^{-}} \mathrm{P} \qquad (10)$$

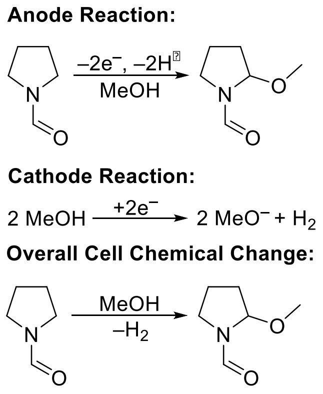
A selective conversion therefore requires that the reactive intermediate decays by a single reaction pathway. This is dependent on the rate of intermediate formation (local current density), the reaction environment (solvent, electrolyte, pH, trapping molecules) and temperature. For example, oxidations should be carried out in the presence of a single or dominant nucleophile. There is a very large literature on organic transformations by electrolysis, but it is only a guide as most of the reported reactions have only been carried out in poorly designed beaker cells with a low conversion. The use of an Ammonite Cell may lead to higher selectivity as well as higher conversion.[5] Particularly useful in assessing the suitability of a reaction in the Ammonite cells is data on the range of potential for the oxidation/reduction of functional groups in the reactant and products in the medium planned for the synthesis. These may be available in the literature or can be determined by cyclic voltammetry.

8.2 Cell Chemistry

When planning a synthesis in an Ammonite Cell, it is important to think about the total chemical change in the cell. ***In terms of electrons, the amount of chemical change at the counter electrode is the same as that at the working electrode***.

Clearly, a high selectivity requires a clean reaction at the working electrode for all reactant concentrations and reaction environments met along the flow channel. In addition, however, in these undivided microflow electrolysis cells, it is critical to consider the overall chemical change in the cell including that at the counter electrode. It is also essential that the counter electrode chemistry does not interfere with the reaction at the working electrode and its rate does not limit the cell current. Failure to include the counter electrode in the consideration of the chemistry can lead to a complex mixture of products (eg. the reactant may be electroactive at the counter electrode and/or solvent/electrolyte degradation may lead to unwanted organic products) as well as a situation where the environment close to the working electrode varies strongly along the microflow channel.

On the other hand, the counter electrode chemistry can be used constructively to enhance the synthesis performance. For syntheses involving an oxidation, hydrogen evolution is a convenient counter electrode reaction. The gas evolution increases the mass transfer coefficient but, more importantly, can maintain the solution pH constant along the channel. For example, with methoxylation of *N*-formylpyrrolidine (Scheme 1).



Scheme 1 – *Overall cell chemistry occurring during the methoxylation of N-formylpyrroldine.*

The reaction of interest at the anode generates two moles of protons for every mole of reactant converted to product. But the cathode generates two moles of base (MeO^-) preventing the electrolyte going acid as it passes along the channel. Other examples of the application of this strategy have been described.[3] Other strategies include (a) designing a paired electrosynthesis,[5,6] where two ‘non-interfering’ but desirable conversions are carried simultaneously at the two electrodes (b) using a ‘non-interfering’ sacrificial reaction at the counter electrode – an example that can work well for cathodic syntheses is the use of a dissolving metal anode.[7]

8.3 Reactions Studied in Southampton

Reactions demonstrated to give good performance in extended channel length microfluidic electrolysis cells include:

- methoxylation of *N*-formylpyrrolidine [2,9]
- conversion of 4-*tert*-butyltoluene to 4-*tert*-butylbenzaldehyde [3]
- cyclisation via intramolecular alkoxylation [3]
- selective monofluorination [3]
- generation of cerium(IV) [3]
- the Kolbe reaction [3]
- TEMPO mediated conversion [10]
- *N*-Heterocyclic Carbene mediated conversion of aldehydes to esters and amides [11, 12]

9. Choice of Electrolysis Parameters

Key parameters are the concentration of reactant, the flow rate of the reactant solution, f ($cm^3\ s^{-1}$) and the cell current, I_{cell} (A).

The concentration of reactant and the flow rate will determine the target rate of product formation (rate = *cf).* Once the flow rate is chosen, equation (2) can be used to select a cell current for initial electrolyses. Alternatively, the cell current may be determined experimentally

(a) from a plot of cell current against cell voltage while reactant solution is passing through the microflow channel. Such plots can be obtained either by linearly scanning the cell voltage while measuring the current or manually changing the cell voltage in steps and noting the current at each step. Such plots of cell current vs cell voltage should show a wave for the reaction of interest and then the electrolysis cell current should be set at a value close to the plateau of the wave.

(b) by measuring the conversion and selectivity at several cell currents. The first experiment should be carried out using a cell current calculated from equation (2) and both the consumption of reactant and the selectivity for R to P determined.

Again it should be emphasised that for good results, $I_{cell,mt} \geq I_{cell} \geq I_{cell,minimum}$. In general:

- If significant reactant remains unconverted, it indicates that another electrode reaction is occurring at the working electrode, $\varphi < 1$; probably the mass transfer coefficient is not high enough for the flow rate. If the selectivity is good, the experiment should be repeated with a lower flow rate with a corresponding lower cell current. Alternatively, the cell current could be increased, but this may adversely affect the selectivity
- If the conversion is high but the selectivity is poor, it is worth trying a lower cell current although it may be essential to change the electrolysis medium.

In general, we have found a 0.1 M solution of R is a convenient starting point with new systems. Possible electrolysis parameters for a first electrolysis are in the table:

Cell	**c_{in} / mol cm^{-3}**	**f/ $cm^3\ s^{-1}$**	**Suggested cell current/A**	**Theoretical product formation rate/ mol $hour^{-1}$**
Ammonite 8	10^{-4}	1/60	0.33	6×10^{-3}
Ammonite 15	10^{-4}	5/60	1.7	3×10^{-2}

Table 3 – *Suggested conditions for a first electrolysis with a 2 e^- reaction.*

The product formation rate can then be increased by increasing either the reactant concentration or the solution flow rate but both changes require a proportional increase in cell current. Using an increased flow rate also requires that the mass transfer coefficient is high enough that R to P is the only anode reaction.

10. Performing a Reaction in the Ammonite Reactor

Step 1 – Consider the chemistry and select appropriate conditions

For successful electrosynthesis before commencing any chemistry in the Ammonite reactors ensure the overall chemistry occurring at both the working and counter electrodes has been considered. Also, consider the amount of product required and at what rate, as this enables selection of appropriate solution concentration and flow rate, which leads to suitable current to be applied. ***See sections 4 to 7 for how information on how to select the appropriate conditions.***

Step 2 – Clean and polish electrodes

The stainless steel electrode and carbon filled PVDF electrode need cleaning and polished between experiments. First rinse both electrodes with organic solvents to remove organic contaminants. Then polish the electrodes in a smooth circular motion with cotton wool to remove any build-up of material (see figure 4). Finally, the carbon filled PVDF working electrode can be polished with a polishing cloth and silica:

1. First take the polishing cloth add a spatula of silica (the smaller the particle size the smoother the electrode surface will be) and wet with water.
2. Then rub the polishing cloth loaded with wetted silica over the electrode surface in a smooth circular fashion, to remove the top layer on the electrode (see figure 4).
3. The rinse the electrode and dry. The electrode is then ready to use.

A regular cleaning and polishing routine will help maximise the lifetime of the electrodes. ***Note – The carbon filled PVDF electrode should be considered as a consumable part of the reactor. Eventually, it will need replacing. Running electrolysis at higher current will reduce the electrode's lifetime.***

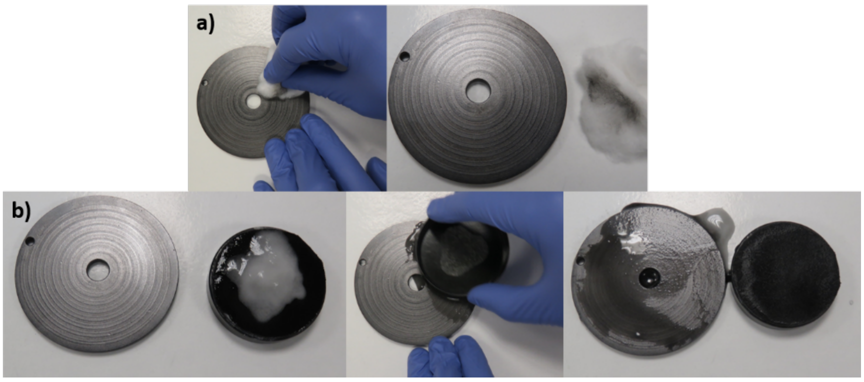


Figure 4 – a) Polishing the electrode with cotton wool. b) Polishing electrode with polishing cloth and silica gel.

Step 3 – Construct the Reactor

First place the recessed stainless steel electrode onto the base plate (see figure 5). Next place the gasket (spacer) into the recessed groove. Ensure the gasket does not block the inlet/outlet holes as this can lead to blockage and subsequent leakage. Run a finger over the gasket to ensure a good fit into the groove. Insert the insulation sleeve around the central bolt hole. Then place the polished carbon electrode on top of the gasket. Next place the copper contact plate on top of the carbon electrode. Finally place the Perspex top plate on top, ensuring the screws line up with the base plate. Then tighten the screws with an Allen key for the Ammonite 8, or using a torque wrench for the Ammonite 15 (outside bolts 4 Nm, central bolt 20 Nm).

Figure 5 – *Steps illustrating the construction of the Ammonite reactors.*

Step 4 – Connect to Pump

The Ammonite 8 and 15 can be connected to any pump or existing flow set-up by standard fixtures and fittings (see figure 6). Once connected to a pump, flow a solvent solution through the cell, looking for any leakages (if pump has a pressure sensor, ensure there are no pressure rises, which are indicative of a blockage). It is good practice to check the flow rate to ensure the pump is performing correctly. ***See troubleshooting for advice on leakages.***

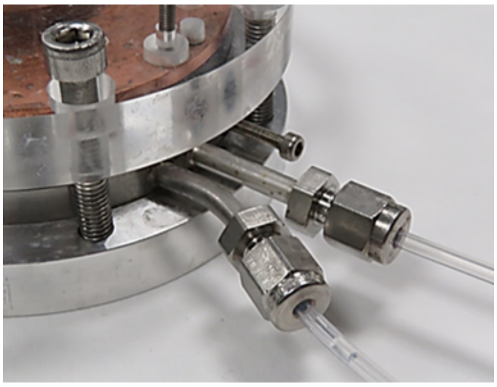


Figure 6 – *Picture of the tubing connection for the Ammonite 8 reactor.*

Step 5 – Connect to a Power Supply

The Ammonite 8 and 15 are designed to work with a range of power supplies (ensure power supply, wiring and clips can deliver and handle required current). Connection is made via crocodile clips to the electrical contact sites (see Figure 7). Ensure the contacts are the correct way round. For an oxidation the working electrode is acting as the anode so should be connected to the positive terminal (typically the red wire), the counter electrode is acting as a cathode and needs to be connected to the negative terminal (typically the black wire). If the desired reaction is a reduction, the connections need to be reversed.

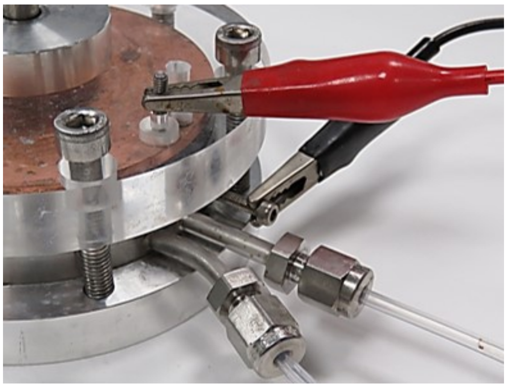


Figure 7 – *Picture of electrical contacts for the Ammonite reactor.*

Step 6 – Turn on Power Supply

First, ensure power supply is set to operate in constant current mode and ready to deliver the required current (different power supplies have different methods of doing this). Then turn on the power supply. At this point the current reading should be 0 (or very low, depending on the sensitivity of the power supply) and the voltage reading high, because no reactant (electrolyte) solution is passing through the reactor, just solvent. This means almost no current is flowing at the moment. ***If a current is observed at this point see troubleshooting.***

Step 7 – Pass Reactant (Electrolyte) Solution through Cell

Depending on your flow set up, begin to pass the reactant solution through the cell. When the reactant solution begins to enter the Ammonite cells, the current will begin to rise, until the set value is reached. At this point the power supply will switch to constant current and voltage value will begin to fall, until it reaches a steady state (the voltage value will be dependent on the chemistry being performed). At this point, the Ammonite reactor is fully charged with reactant/electrolyte solution. If the counter electrode reaction produces gas, bubbles will be observed exiting the reactor. ***See troubleshooting if a current is observed, but the voltage is 0 (or very low).*** The reactor will stay at this steady state until the reactant solution has passed. When the Ammonite cell begins to fill with solvent, the voltage will begin to increase up to its set value, then the current will begin to decrease, this is a sign that the reaction has finished.

Step 8 – Dismantle Cell

On completion of the reaction, dismantle the reactor (follow the reverse of step 3). When dismantling the reactor, inspect electrode for evidence of damage. Then repeat sequence for subsequent reactions.

11. Troubleshooting

The Ammonite 8 and 15 are robust reactors, but on occasion problems may occur. Most issues can be resolved by the following advice.

11.1 Leakage

Leakages generally occur when a blockage prevents the flow of solution, leading to a rise in pressure, which can cause leaking at the weakest part of the system. If the system has a pressure sensor, the increase in pressure can be observed. The location of the leak can be helpful when trying to find the blockage, as the leak can only occur upstream at the weakest point from the blockage (typically at a tubing connection, or the gasket slipping out of the Ammonite reactor).

The Ammonite 8 and 15 have been designed to have large bore inlet and outlet tubes to reduce the risk of blockages. It is good practice to inspect the inlet and outlet and clean regularly. Cleaning can be achieved by flushing the system with solvent. It is good practice to avoid leaving reactant solution sitting in the inlet/outlet tubes because the solvent could evaporate leaving behind reagents and/or electrolyte causing fouling, which could lead to a blockage.

The most likely cause of a blockage in the Ammonite reactors is due to accidently blocking the inlet and outlet holes with the gasket. If this occurs, simply dismantle the cell, and then reassemble, taking care to ensure the inlet/outlet holes are not blocked. If leaking persists try changing the tubing connected to the Ammonite reactor. Finally if leaking from the Ammonite reactor persists, inspect the quality of the carbon electrode. Sometimes after extensive use, small cracks can appear which can lead to leaking. The carbon electrode will then need to be replaced.

11.2 Electrical Shortage

An electrical shortage occurs when a bridge or contact has been made between the two electrodes. This allows the current to flow through the path of least resistance, meaning the current is not passing through the reaction solution, leading to no conversion.

An electrical shortage can be diagnosed from the power supply display, and/or observing the exiting solution. When an electrical shortage occurs, the power display often shows that the selected current is being passed, but with a very low voltage, typically < 1.0 V (***Note – The voltage will be dependent on the chemistry occurring, the electrolyte loading, flow rate and temperature, but in most cases is typically >2.0***

V, when operating correctly). If an electrical shortage is suspected, check the reaction solution exiting the cell. If your chemistry generates gas evolution or a colour change for example, this should be observed leaving the cell. If cell chemistry is observed, then the reactor is fine, the reaction just occurs at a low voltage. If no cell chemistry is observed, then it is likely an electrical shortage has occurred.

The most common cause of an electrical shortage is a contact being made between the two electrodes (eg. due to carbon particles resulting from corrosion/erosion of the carbon filled PVDF anode). Therefore if an electrical shortage is suspected, turn off the power supply and dismantle the reactor. Clean and polish the electrodes, and inspect the wiring and connections to the reactor. Then reassemble and try again. In most cases this fixes the electrical shortage. Sometimes the electrical shortage can be indicative of the carbon electrode becoming defective, therefore a replacement electrode will be required. Finally if the problem persists, it has been observed, in some rare cases, that the chemistry causes the electrical shortage, by causing polymerisation on the electrode surface, which leads to a contact being made. In these cases the cell chemistry needs to be reconsidered to address this problem.

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