SCHOOL OF ELECTRICAL ENGINEERING
AND TELECOMMUNICATIONS

Low Technology Integrated Circuits

by

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Abstract

This thesis aims to develop an integrated circuit technology that is affordable and practical enough to be used in secondary and tertiary education. All existing teaching techniques are either severely limited in terms of appropriateness or accessibility.

The challenge in this task is the development of semiconductor-like devices using commonly available ingredients and "low-technology" processes.

The primary focus of this part B paper is attempting to create a "useful" macro-scale transistor. This goal is not met, however many other interesting areas of research are uncovered and the limits of an IC technology using only diodes are explored.

Terminology

AER Aluminium Electrolytic Rectifier. The most common variant of an electrolytic rectifier using aluminium as the cathode, see section §4 for more information.

baking soda A mixture of sodium hydrogen carbonate, a powdered acid and other filler compounds such as rice flour. Not to be confused with "bicarb soda".

bicarb soda Sodium hydrogen carbonate, or "sodium bicarbonate". Not to be confused with "baking soda". Chemical formula: $NaHCO_3$

dopant A material added in a small quantity to another material to (often drastically) change its electrical properties.

electrolyte A solution (mixture of water and a dissolved material) with electrically conductive properties.

FET Field Effect Transistor. A popular type of transistor where a voltage applied to an insulated gate electrode changes the behavior of the device.

IC Integrated Circuit. A collection of circuit elements (resistors, capacitors, transistors, diodes, etc) assembled on a (typically small and flat) substrate to create a new device. This device performs a function greater than any of its individual components.

ion-selective electrolyte Synonym for "ion-selective membrane".

ion-selective membrane A porous substance that interacts with certain dissolved ions in specific ways.

OECT Organic Electro-Chemical Transistor. A type of ionic transistor that acts similarly to a FET but uses electrolytes instead of semiconductors and insulators, see section 2.2.3.

PCB Printed Circuit Board. A board (commonly made of fibreglass) with electronic circuit components etched and soldered onto it.

redox A category of chemical reactions involving "reduction" and "oxidation". These processes involve the acceptance or removal of electrons.

SCL Semi-conductor-like. An SCL material or SCL device behaves like a semiconductor, but may internally use processes different to traditional semiconductors to achieve this goal. Any material that can be used to make a diode or an amplifying device is considered an SCL material.

transistor A single electronic device with amplifying properties. Debate exists on whether or not the term “transistor” only applies to amplifiers using traditional semiconductors, however the term has been expanded in modern times to cover various off-the-shelf non-silicon devices.

electrolysis The forcing of a chemical reaction through the external application of electricity.

In this thesis the term electrolysis is primarily used to refer to the splitting of water into hydrogen gas and oxygen gas, observed as small bubbles appearing on metal electrodes under water when a voltage is applied.

$NaHCO_3$ Chemical formula for sodium bicarbonate. See “bicarb soda”.

Contents

1 Introduction

1.1 Problem

Existing Integrated Circuit (IC) fabrication technologies are unsuitable for large-scale practical teaching. Traditional methods are expensive (requiring cleanrooms, specialist equipment and extensive staff hours) as well as dangerous (requiring hydrofluoric acid, toxic metal compounds, etc).

Most students instead learn IC development through computer simulation. A select few then obtain the privilege to access real fabrication facilities.

Simulators are useful teaching aids, however on their own they are difficult for beginner students to engage with. They are completely "virtual", with no tangible inputs or outputs other than diagrams and numbers. Simulation is most effectively used as a teaching tool in tandem with hands-on experimentation, not in replacement of it.

Printed circuit boards (PCBs) are a limited and labour-intensive alternative to IC fabrication. Many problems faced in traditional IC fabrication are not modeled due to the use of pre-tested and parameterised off-the-shelf parts. The iterative PCB design, ordering/manufacture and soldering processes are lengthy, especially for beginners, taking up time periods impractical for most educational schedules that last only weeks to months.

A simple and low-technology IC fabrication technology is required.

1.2 Components of an Integrated Circuit

To be comparable to traditional IC fabrication techniques an analogous process requires at minimum:

1. A substrate
2. Resistors
3. Capacitors
4. Diodes
5. Transistors

Diodes and transistors are the most difficult of these components to construct, as they require semi-conductor-like (SCL) behaviors and tighter dimensional tolerances. Inductors are not strictly required for IC design; they often avoided or simulated with other components instead.

1.3 Hypothesis

I believe that low-performance integrated circuits can be manufactured using macro-scale, "low technology" techniques and ingredients. The limiting factor that has prevented a method being developed is cultural rather than technological.

Materials with SCL properties are abundant in our everyday lives. Copper oxides[1], iron oxides[2], the plasma in fluorescent tubes, electrolytes in capacitors, galena bearing stones found in gardens[3] and even carbon microphones[4]. The difficulty is not in finding the materials or proving their SCL properties, but in the design of systems that reliably exploit them to make diodes and transistors.

Research into semiconductors and integrated circuits since mid-last century has focused on pursuing techniques and chemistries with the highest possible electrical performance, at the cost of other factors. As a result most modern processes use high-upfront cost manufacture techniques requiring "high-technology" processes such as lithography and vacuum deposition; as well as dangerous chemicals such as hydrogen fluoride.

A monoculture of information has lead to many modern engineers believing that it is prohibitively complex and expensive for an individual to manufacture semiconductors or integrated circuits. It is difficult to consider education or experiment-focused IC design processes because we are almost exclusively exposed to mass-manufactured ICs and the goals of mass-manufacture products. Even educational literature focuses exclusively on “high-technology” IC fabrication because of its end-goal commercial appeal.

The difficulty of creating a low-technology IC fabrication technology is not in finding low-technology semiconductors, but instead developing ways of making them easy to use for the target audience.

1.4 Aim

To develop a low-quality IC fabrication technology that is:

1. *Accessible* for use in education (low-cost, reduced toxicity)
2. *Relevant* to traditional IC development and production (similar construction methods, analogous dimension/design/performance problems, etc)

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[1] “Cupric” or “cuprous” oxide rectifiers were used commercially for power rectification in the early 1900s. The two variants of oxide are (incorrectly) written interchangeably in many texts.

[2] Famously used to build “foxhole radios” in World War II.

[3] “Cat’s whisker” crystal detectors.

[4] “Balance beam amplifiers” (Friedrichs 2003 p64)

3. *Reliable*, so that students can immediately (and repeatedly) make devices that work.
4. *Minimally performant*: no emphasis on IC lifetime or operational speed, only that the devices work.

1.5 Overview of SCL Solutions Investigated

- "Home-technology" metal oxide devices.
- "Home" attempts to perform traditional solid-state transistor fabrication at a lower cost.
- Point contact devices, including point contact diodes and transistors.
- Ionic devices, including as macro-scale electrolytic rectifiers and micro/nano-scale ionic transistors.

1.6 Results

Achieved:

- "Low technology" IC substrates and passive electronic components (section 2.3).
- "Low technology" diodes, using miniaturised and simplified electrolytic rectifier technology.
- "Low technology" lookup-table logic using diode matrices, with a working demonstration performing digital logic (limited, non-turing without transistors) (section 4.3).
- "Low technology" light emitting ionic devices (limited, requiring high voltage AC) (section §7).
- Formal testing procedure for determining if a transistor or amplifier is "useful" for traditional purposes. (section §5).

Not Achieved:

- A working macro-scale transistor technology valid for "low-technology" IC development.

Other conclusions:

- The Aluminium-NaHCO3 technology that works for ionic diodes is likely fundamentally incompatible with transistor-like operation.
- Many published papers claiming the development of unusual transistor-like devices actually demonstrate attenuators. The definition of "transistor" is widely interpreted across the sciences its definition has changed over time.
- Field-effect transistor devices cannot be scaled up to macro-scale without the application of extreme voltages.

Future research avenues for "useful transistors":

- Concentration control transistors using chemistries other than Al-NaHCO3 (4.1.2). Eg Ferric-Ferrous sulphate couple devices (Letaw 1954).
- Bubble-control transistor devices (a mode/method of operation potentially practical with macro-scale ionic devices) (section §8.1).

1.7 Relationship to Part A of this thesis

Where appropriate sections of part A have been brought over or summarised in part B. Part B intends to stand on its own, however some content has been omitted where appropriate for brevity.

A full copy of part A is available online at:

`http://halestrom.net/misc/thesis1819/partA.pdf`

Author note: halestrom.net is spelt "strom" not "storm", misspelling the URL will prevent this document from being accessed.

Part I

Research

2 Important research and findings from Part A

2.1 Non-electrolytic IC fabrication alternatives

2.1.1 Adapting traditional IC fabrication to home environments

Several individuals have attempted to recreate commercial semiconductor fabrication techniques in their own homes. Their aims are to adapt the well-researched methods of traditional IC manufacture to a lower cost and more accessible format.

Unfortunately most of these attempts have resulted in processes that are difficult and dangerous (inappropriate for the goals of this thesis) and perform poorly (limiting their usefulness even as traditional ICs). To date no-one has overcome these problems, suggesting that adapting commercial IC processes is a difficult and inappropriate pathway for this thesis. Examples include:

- Ellsworth (2010), who created transistors using silicon wafers bought from the internet, masking techniques and home kilns. The final products exhibited poor gain and required extensive manual bonding processes to attach to external circuits.
- Barnekow *et al.* (2012), who attempted to replicate Ellsworth's experiments in creating FETs using ingredients sourced from the internet. They suffered equipment damage, fires, poor yield due to impurities and unreliable results.

2.1.2 Point-contact and other exotic SCL devices

A wide variety of simple-to-manufacture devices exhibit SCL properties, including (Friedrichs 2003):

- Unstable contact amplifiers
- Magnetic amplifiers
- Vacuum tubes
- Point contact diodes and transistors

These devices are easy to make and require common ingredients, making them an appropriately accessible technology. Unfortunately all of these devices require delicate or complicated construction and adjustment, making them inappropriate for integrated circuit development:

- Unstable contact amplifiers require complex physical components and balancing to achieve only narrow-band AC amplification, severely limiting the circuits that can be made with them.
- Magnetic amplifiers are a robust and proven technology (Steiner 2009), but do not teach concepts analogous to traditional integrated circuit development processes.
- Vacuum tubes are analogous to JFETs, but require dangerous and slow glass-working and vacuum techniques to make.
- Point contact diodes are often delicate and sometimes require constant mechanical adjustment (Hales 2017, Friedrichs 2003).

None of these technologies meet the criteria set out in section 2.1.

The next section of this report instead investigates the more promising "ionic" or "electrolytic rectifier" technologies, which appear to be more suitable for adaption to "kitchen" or "classroom"-scale technology.

2.2 Micro and Nanoscale Ionic Transistors

Over the past two decades several types of ionic transistor have been developed, where ions are used instead of electrons in all of or part of the operation of switching devices. Existing ionic transistor technologies were investigated to determine how AER or similar chemistries could be applied to create transistors. Each technology was assessed on its:

- Need for exotic materials
- Dimensional and process requirements

2.2.1 Ionic Bipolar Transistors "iBJTs"

Tybrandt (2010) investigated devices that use two different types of ion selective membranes to simulate N and P doped traditional semiconductors. Due to the similarity between these devices and bipolar junction transistors (BJTs) Tybrandt identifies them as "iBJTs".

Ion selective membranes are typically exotic and complex substances that electronically interact with only certain types of ion in solution. Tybrandt designed and tested devices using "Fumatech FAB", a proprietary membrane, and "PEDOT-PSS" (polystyrene sulphonate), a modified (doped) variant of "PEDOT" (a polyethylene dioxide derivative). Neither of these materials are suitable for "low-technology" purposes.

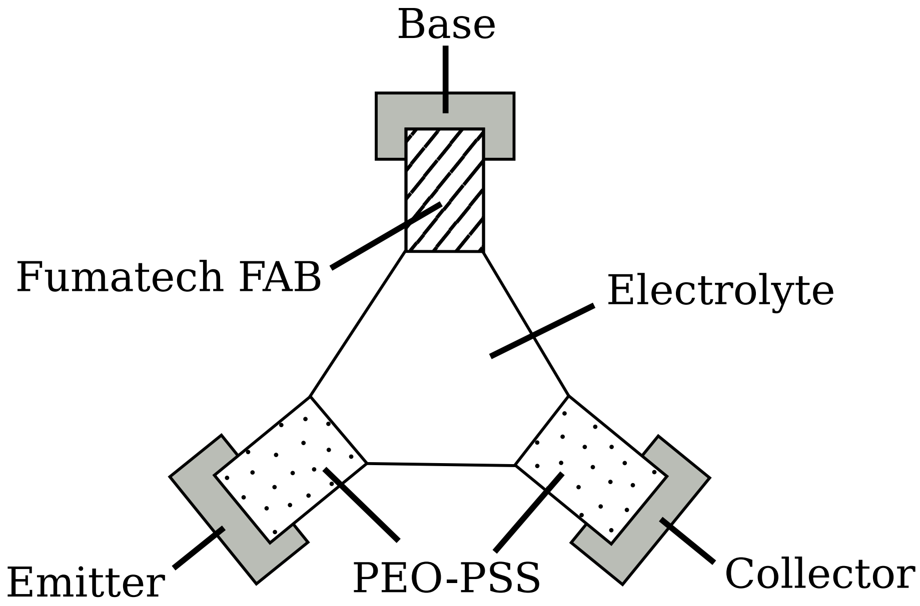

Figure 1: iBJT physical structure.

iBJTs have a physically simple structure (see figure 1) but their method of operation is extremely complex. To obtain the desired charge levels and behaviours at each terminal (exchange membrane) a variety of complex ion exchange processes take place simultaneously inside the device.

iBJT based designs are inappropriate for the aims of this thesis due not only to their “high technology” material requirements, but also because of their inability to be related or adapted to simpler processes and chemistries such as those used in AERs.

2.2.2 Hybrid channel modulators

A traditional field-effect transistor (FET) is composed of a conductive channel that can have its conductivity controlled (modulated) and a conductive gate that controls this channel. Between them lies an insulator to provide isolation, commonly an oxide.

A hybrid channel modulator replaces the isolation layer with an electrolyte. Inside the electrolyte ions can move, however they cannot leave the electrolyte and enter the channel or the gate. A structural diagram is in figure 2 (a).

From an external perspective hybrid FETs appear to operate the same way as a normal FET, but internally charges are pushed and pulled using a stage of charged ions inside the electrolyte. Parts (b) and (c) of figure 2 show the charge carriers inside the conductive channel being manipulated by the the charges in the electrolyte to modify the conductivity of the channel. A channel cannot conduct in regions where it does not contain carriers.

These devices are being investigated by the Nano-Electronics team at UNSW (Ullah 2018). Whilst it is possible to make these devices using traditional planar processes, they

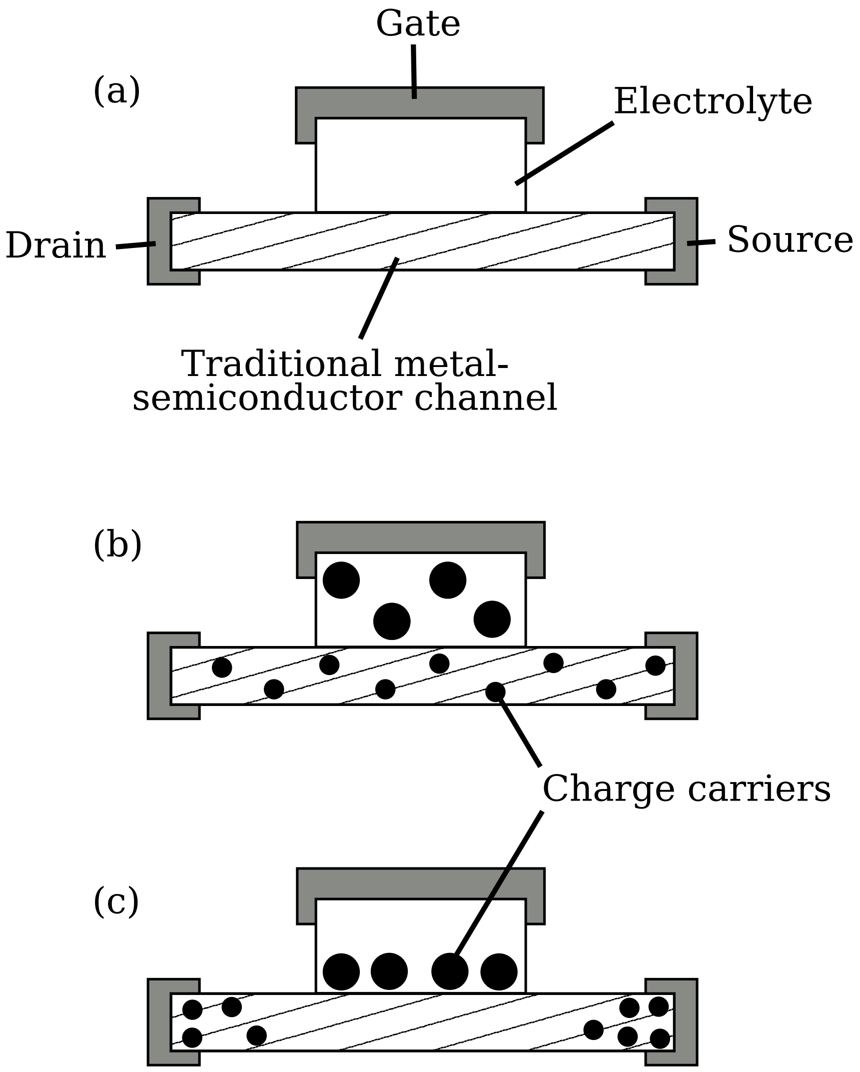

Figure 2: Hybrid channel modulator. (a) internal structure, (b) conductive operation (gate unbiased), (c) non-conductive operation (gate biased)

are instead focusing on the use of nanowires as the conductive channel and investigating higher-than-normal doping concentrations.

The replacement of the insulating layer on the gate of the FET makes these devices easier to manufacture at a macro scale. Gate oxides are dimensionally important, whilst electrolytes can be larger than necessary and still conduct charges to each end.

Unfortunately these devices are still inappropriate for use as a “low-technology” transistor, as they require the use of a traditionally doped semiconductive channel, which is outside the technological scope of processes this thesis aims to use.

2.2.3 Organic Electrochemical Transistors (OECTs)

OECTs go a step further than hybrid channel modulators by replacing both the gate oxide and the channel with electrolytes, see figure 3 (a).

The channel is replaced with an ion-selective electrolyte to simulate a doped semiconductor (Khodagholy 2013). Carriers from the inert gating electrolyte enter the channel and “cancel” the mobile carrier charges to make the channel non-conductive, see figure 3 (c).

Khodagholy’s motivations are to demonstrate devices that have much higher transconductance (g_m) than traditional transistors, however these performance gains are not relevant to the topics of this thesis.

Whilst these devices still require the use of exotic compounds (ion-selective membranes) they have less strict requirements on dimensional control and do not require traditional semiconductor materials. This makes them a valid option for extending and adapting for use in a “low-technology” form, assuming the materials can be replaced.

2.2.4 Redox diffusion devices

Letaw (1954) describes devices intended for use as a slowly-operating educational analogs to traditional transistors. They operates based on redox reactions and the diffusion of ions across a small gap.

The device is composed of (figure 4):

- Collector an emitter: Two non-reactive and insulated electrodes spaced less than 500um apart, with their facing surfaces exposed.
- Base: An electrolyte-reactive electrode spaced a comparatively large distance away.
- An electrolyte spanning both of these devices, chosen to be a correct couple for the reactive electrode.

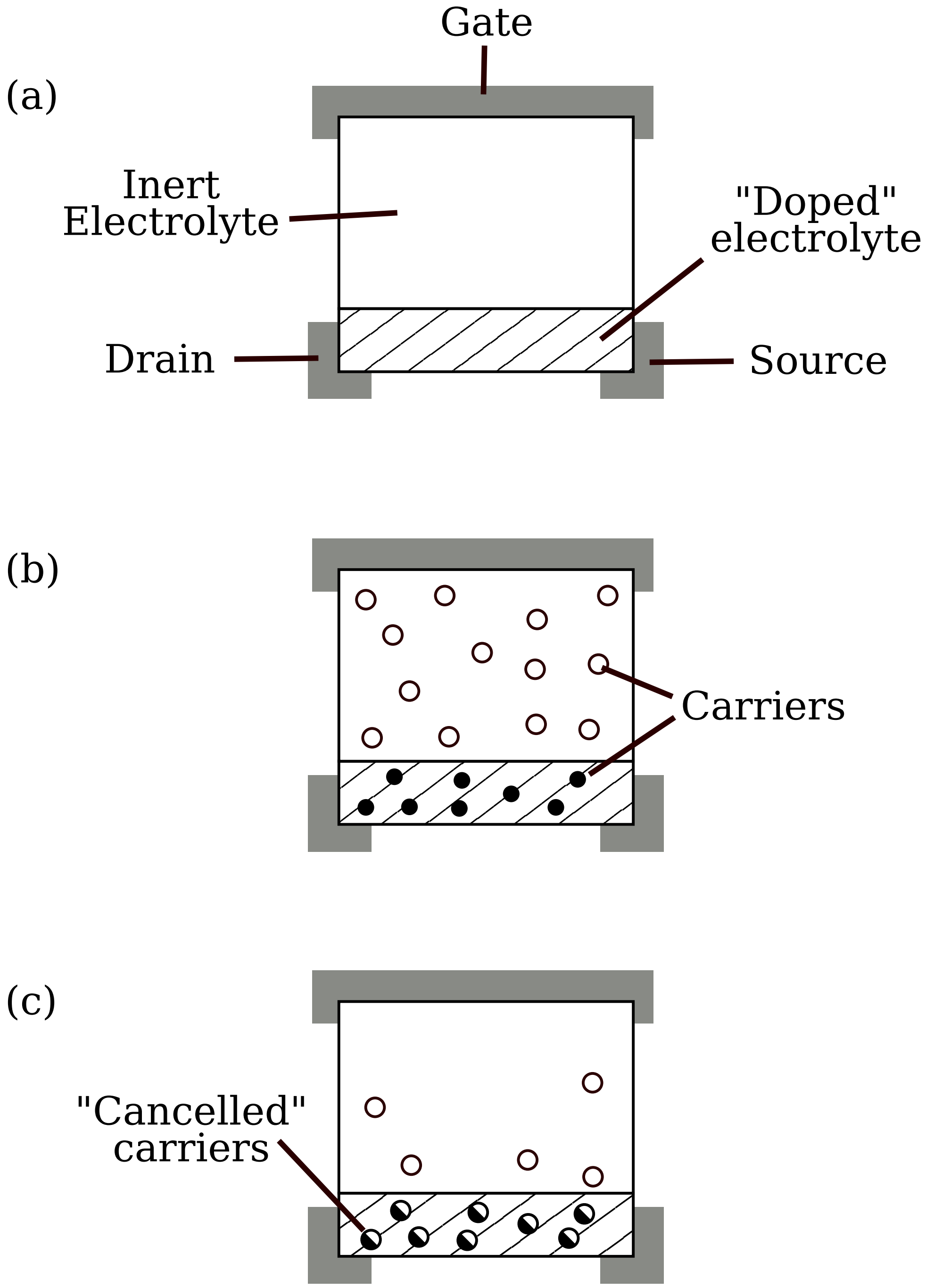

Figure 3: OECT (a) physical structure, (b) conductive state (gate unbiased), (c) non-conductive state (gate biased)

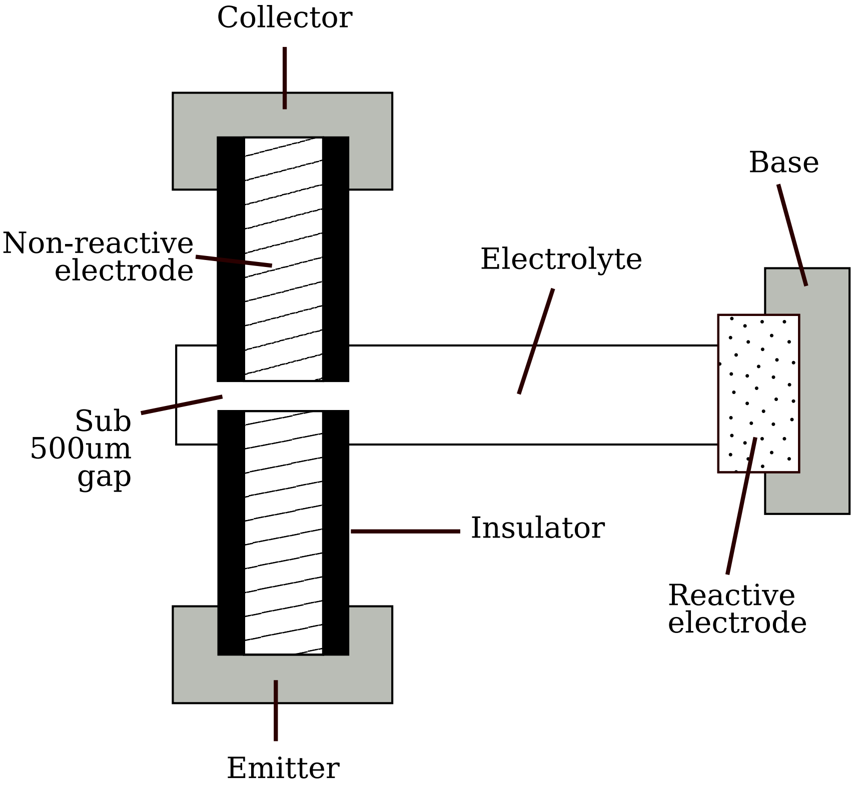

Figure 4: Redox diffusion device

The device will conduct if the right ion species are available in the electrolyte in the correct quantities. Particles on one electrode are ionised, then diffuse to the other electrode to de-ionise. This process conducts electricity from one side to the other by exchanging electrons in one direction with charged particles traveling the other. The reactive electrode is distanced far enough away to avoid participating in any tunneling or direct-diffusion effects.

The mixture of ion species in the solution is modulated using the reactive electrode. This electrode partially dissolves in and out of the solution when changing solution concentrations, and these concentration changes modulate the processes in the small gap between the two main electrodes.

Letaw describes the devices as being extremely slow, requiring one second or more to transition between on and off. He explains is due to the relative sizes of the dissolved ions used in this transistor compared to the size of electrons in traditional (period: germanium) devices. This explanation is now dubious, considering that since then other ion-based transistors have been proven to operate at much higher speeds (Ullah 2018).

These devices are highly appropriate for adaption to “low-technology” integrated circuits as:

- They are already proven to be operable at a macro-scale.

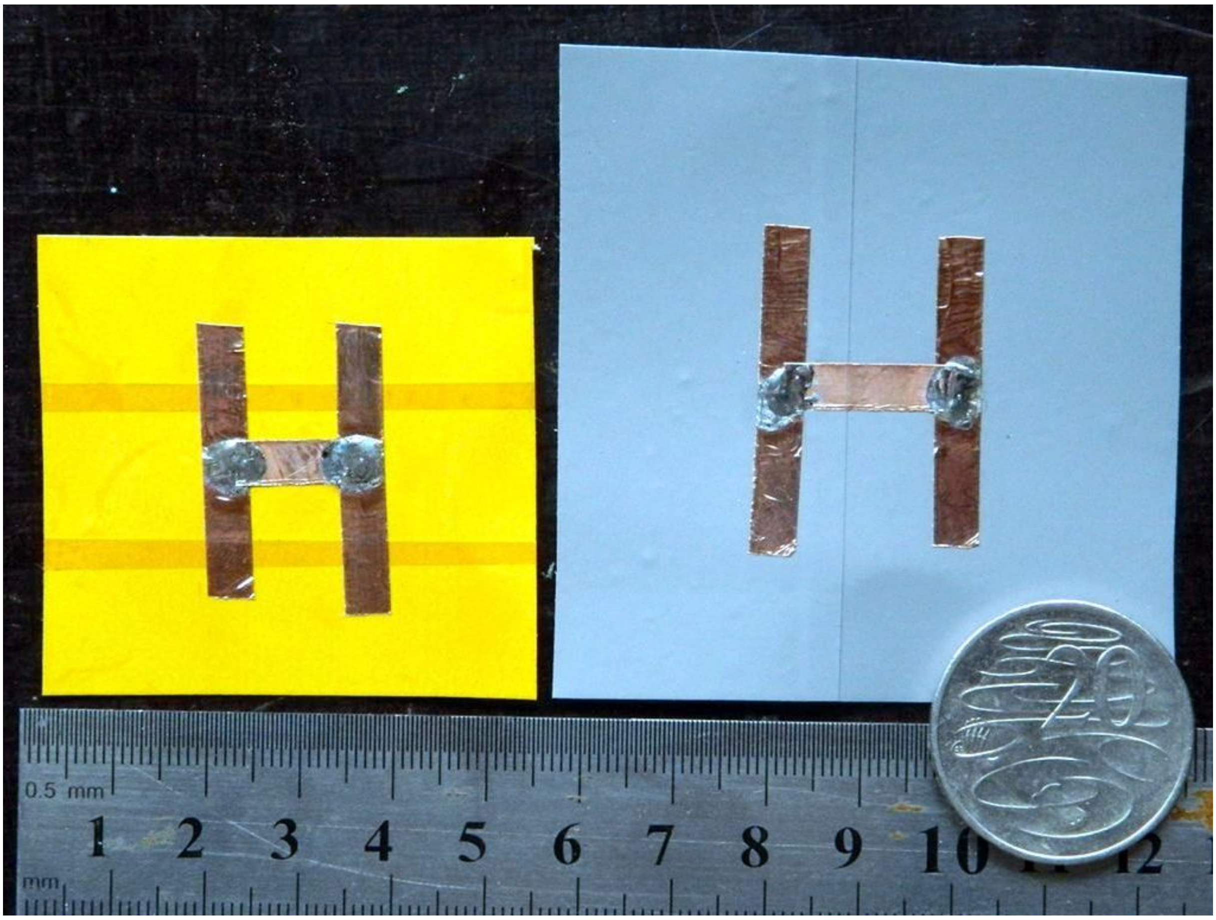

Figure 5: Two substrates supporting copper tape tracks. Left: Polyamide tape ("Kapton") on paper. Right: duct tape on paper.

- They only require one non-macro dimension, which could be fabricated using simple techniques such as knife-cuts.
- A variety of known, functional chemistries are provided by Letaw.

Due to the similarity between redox diffusion devices and AERs it may be possible to adapt an AER to operate as a redox diffusion. This is attempted in section 6.4.

2.3 Passive IC components

Substrate A reliable and easy to make alternative to printed circuit boards can be made using ordinary cardboard and adhesive copper foil (Huang 2018). Junctions are made by using small amounts of solder between overlapping pieces of copper tape. This technique provides an affordable and simple substrate appropriate for educational contexts, but its porous nature prohibits the usage of liquid-based AERs on its surface.

Further development was performed by testing several methods of sealing the cardboard (figure 5). Initially high-temperature resistant polyamide tapes were used (a product

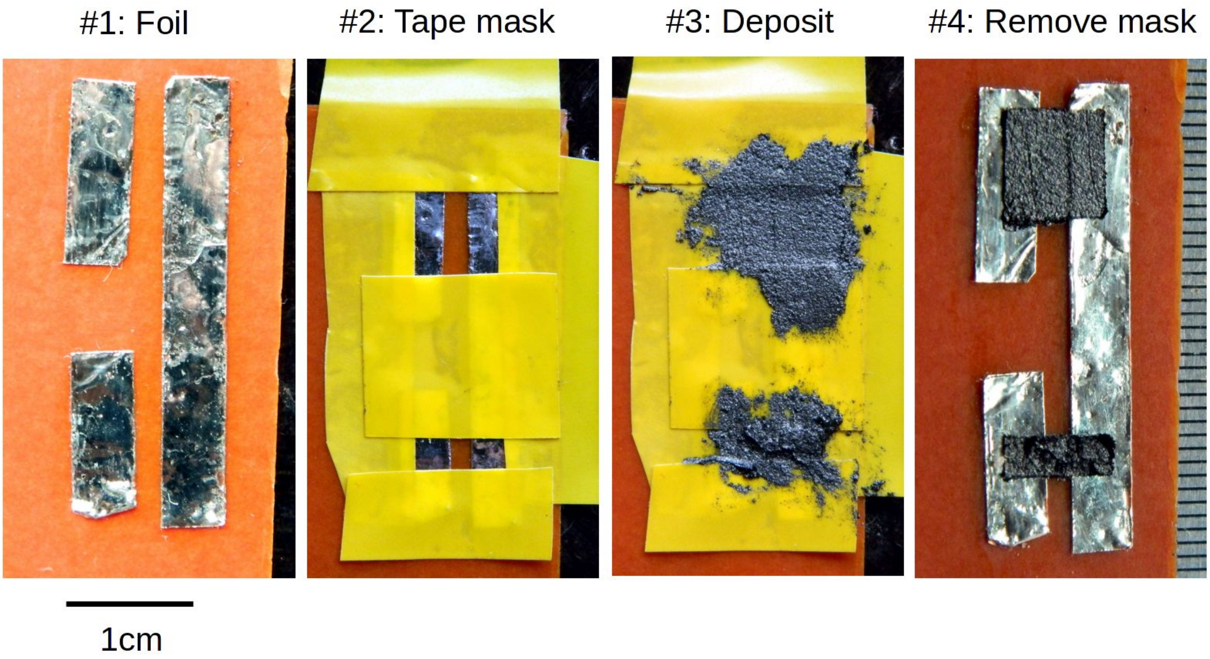

Figure 6: Masking and layup process for resistors.

popular in the electronics industry), however further testing revealed that common duct tape and clear tapes could also survive soldering conditions long enough to provide a reliable substitute.

Resistors Two formulations of resistor were developed:

- Graphite powder[5] in a clay-based binder
- Graphite powder in a silicone-based[6] binder

Resistors were applied via a tape masking process to simulate the masking processes used in traditional IC fabrication and to ensure reliable depositions, see figure 6.

Clay-based binder resistors are easier to work with as any excess material can be washed away. Silicone binders permanently mark clothing and are not as appropriate in some educational contexts.

Secondary properties of both types of resistor also emerged during testing:

- Clay-based resistors are humidity sensitive.
- Silicone-based resistors are pressure sensitive.

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[5] Commonly available in consumer hardware stores in small bottles, intended for lubrication of locks.

[6] Clear tube silicone, commonly available in consumer hardware stores. Used for making water-tight seals between kitchen sinks and benches, as well as various bathroom installations. Acetic acid/air curing, mostly non-hazardous.

Both of these properties may have useful applications. Humidity sensitivity can potentially be used to model the aging seen in traditional ICs, turning it into a valuable educational tool for testing circuit resilience. Pressure sensitivity can allow resistors to be modified "on-the-fly", allowing students to vary transistor biasing and circuit behaviors, or provide input similar to button presses with a minimum of effort.

The pressure sensitivity of silicone based resistors allowed their resistance to be varied by a factor exceeding ten using only moderate finger pressure. The two resistors in figure 6 started with resistances of 30Kohm and 7Kohm; but reduced to 2Kohm and 1Kohm respectively when depressed by hand.

Reliability issues with these resistors, especially the clay variant, were encountered and still need to be rectified. The contacts between the resistor and the metal tracks are delicate and can sometimes shatter, rendering the resistors open-circuit.

Capacitors Electrolytic capacitors can be made from AERs due to the similarity of chemistries between them.

In previous experiments the surface area of the aluminium electrode in contact with the electrolyte has been small, in the order of a few square mm, in order to maximise device switching speed (minimise capacitance). For a capacitor the opposite is desired: high surface area.

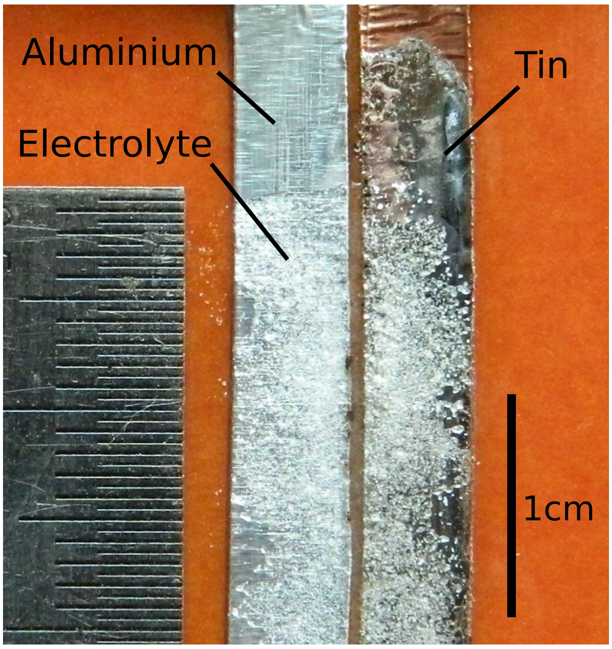

Figure 7: A simple AER capacitor, composed of two metal tape strips that are bridged with an electrolyte.

Simple, non-interleaved arrangements of copper and aluminium tape were tested, as shown in figure 7. Capacitance figures of between $1uF/cm^2$ and $2uF/cm2$ of (“single”) plate area were easily obtained.

More exact and thorough characterisations of capacitive AERs were not performed and the experiments suffered the following limitations:

- Capacitance was measured only at a single frequency by a single device (Extech MN16), so no frequency dependence could be observed.
- Near-field vs far-field effects were not investigated through the use of interdigitated electrodes.
- Experiment was not repeated with a variety of electrolytes types & concentrations, or with varied plate materials.

3 Notable experimental changes since Part A

3.1 Ingredient purity

Although this thesis aims to construct devices using only household-quality ingredients, the use of purer materials permits easier and faster experimentation. Many sample devices in part A would reduce performance over time due to "poisoning" of dissolved metal ions from the metal contacts intended to be non-reactive. Others required special "aging" treatment in contact with the atmosphere (see appendix item 11.1) to operate correctly.

The following new ingredients were obtained for use in part B:

1. 99.95% pure NaHCO3 (purchased from Aldritch through UNSW Physics)
2. $> 1M\Omega.cm$ de-ionised water (obtained from UNSW Physics laboratories or in bottled from hardware stores)
3. Gold leaf (obtained from internet suppliers)[7]

The total cost of these items was around 100 AUD, allowing them to still be considered valid for use in the mass-educational contexts this thesis aims for.

3.2 Equipment

To aid in AC diode experimentation access to a variac (variable AC source) was obtained. This device was primarily used in section §7.

To aid in measurements of multiple circuit parameters during experimentation an array of cheap 830-series clone multimeters was obtained (shown in-apparatus in figure 8). Although these devices are renowned for their poor CAT ratings, poor current modes and poor non-sinusoidal AC integration: they are perfectly adequate for DC measurements if used (and tested) correctly. Each device claims an accuracy of 0.5% +/- 1 digit in their DC volts ranges, which is more than adequate for proving qualitative-goals tasks such as determining whether or not a device amplifies.

3.3 Geometry control

Part A experiments suffered from variation caused by the unreliable dimensions of the hand-assembled devices. Notably the contact area of AERs would vary depending on the size of electrolyte drop/deposit made during construction.

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[7] Gold leaf is particularly cheap due to its low mass, however it is also very fragile and difficult to handle. One handling technique is described appendix item 12.2.

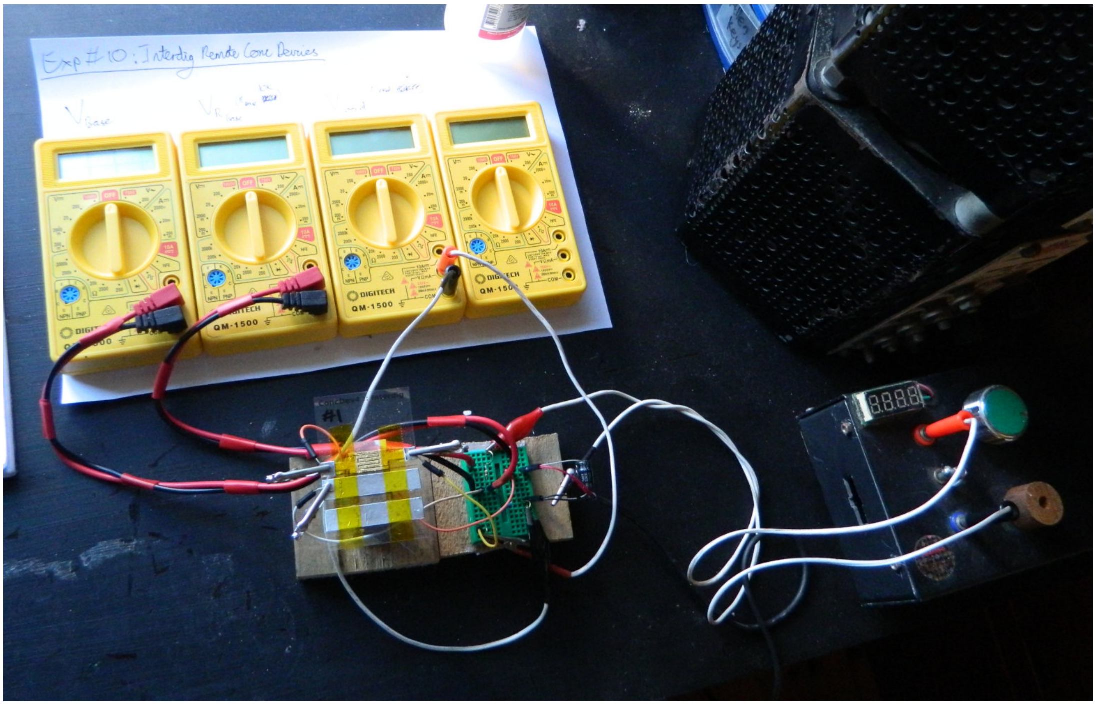

Figure 8: An array of cheap multimeters setup to monitor several parameters of an experiment. Where multiple signals can be measured as stable DC voltages (notably DC currents can be converted to DC voltages through the use of resistors) these cheap devices prove indispensable.

To combat this problem masked stencils were developed using clear overhead projector slides, adhesives, metal tapes and polymer tapes. Stencils were designed on a computer using Inkscape[8] and then printed directly onto the slides using a standard laser printer. The polymer tapes provided a way of limiting the maximum surface area contact that liquids could have with metal electrodes. Examples are shown in figure 9 and figure 10.

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[8] Free software, see https://inkscape.org/

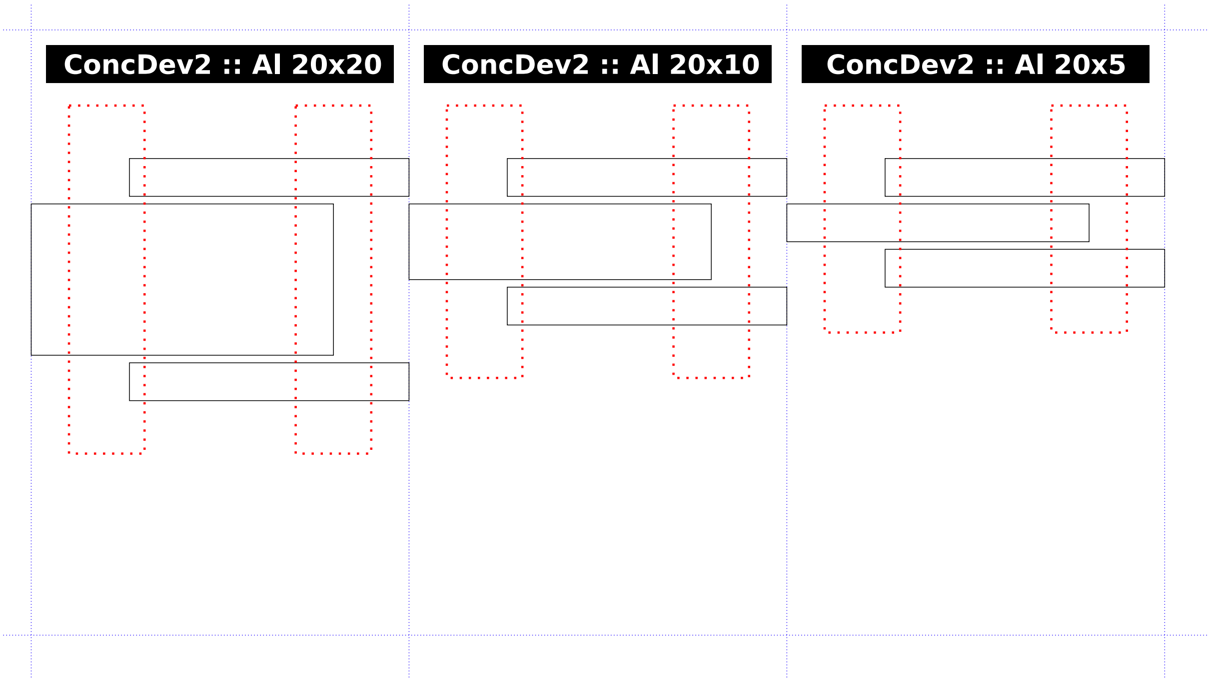

Figure 9: Original stencil templates designed on a computer for printing onto clear overhead projector slides. 1:1 scale if this report is printed 1:1 (marginless) on A4 paper.

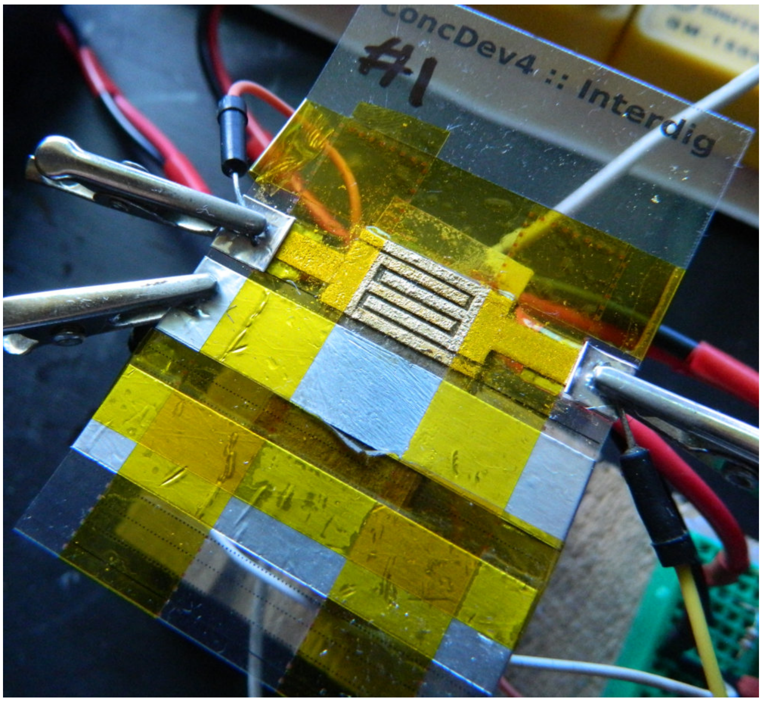

Figure 10: A finished stencil device ready for application of electrolyte drops and experimentation. The yellow plastic tape provides a fluid barrier, containing any drops of electrolyte (not shown) within the central exposed region. The device is otherwise constructed of metal foils adhered to a transparent plastic overhead slide.

4 Aluminium Electrolytic Rectifiers: diodes and research of the junction

4.1 (Part A) Background

In the 1920's the "electrolytic rectifier" was a technology used to convert mains AC to DC for operating radios (Atkinson 1921, Fitch 1926). Silicon diodes had not yet been developed and thermionic diodes (vacuum tubes) were expensive components.

Finding information on electrolytic rectifiers is challenging as little research was made into these devices since the mid 20th Century. In the 21st Century a limited number of individuals have attempted to repeat electrolytic rectifier experiments with varying levels of success (Steiner 2003) or for unrelated and scientifically dubious intentions (Heffner 2006). Areas where information is contradictory, unreliable or dubious are noted relevantly in the sections below.

The concept of using electrolytic rectifiers on a small scale or in integrated circuits appears to be novel, with no prior evidence of adaption to this scale encountered. All literature reviewed in this document focuses on either inspecting particular properties of the rectifier reactions, such as the surface glow or oxide growth, or for bulk-rectification of electricity to power devices, such as radios.

4.1.1 Composition and operation

An electrolytic rectifier consist of three components (Fitch 1926, Atkinson 1921, Kruse 1922):

1. A conductive *anode* made of a material that does not dissolve or react in the solution.
2. An *electrolyte* solution, bridging the anode and the cathode.
3. A *cathode* that reacts with the solution to form an insulating layer on its surface.

An example aluminium electrolytic rectifier (AER) is shown in figure 11. During reverse rectifier operation, where the rectifier is intended to block current, an insulating layer develops on the surface of the aluminium. The exact nature of this film is debated, with some sources assuming it is only aluminium oxide (Shinohara 1952) and others surmising it is a more complex arrangement of aluminium oxide, aluminium hydroxide and a trapped gas layer (Fitch 1926). This layer grows suddenly at first and then slows, peaking at resistance values of megaohms per square centimeter of surface area only after several hours of operation (Shinohara 1952).

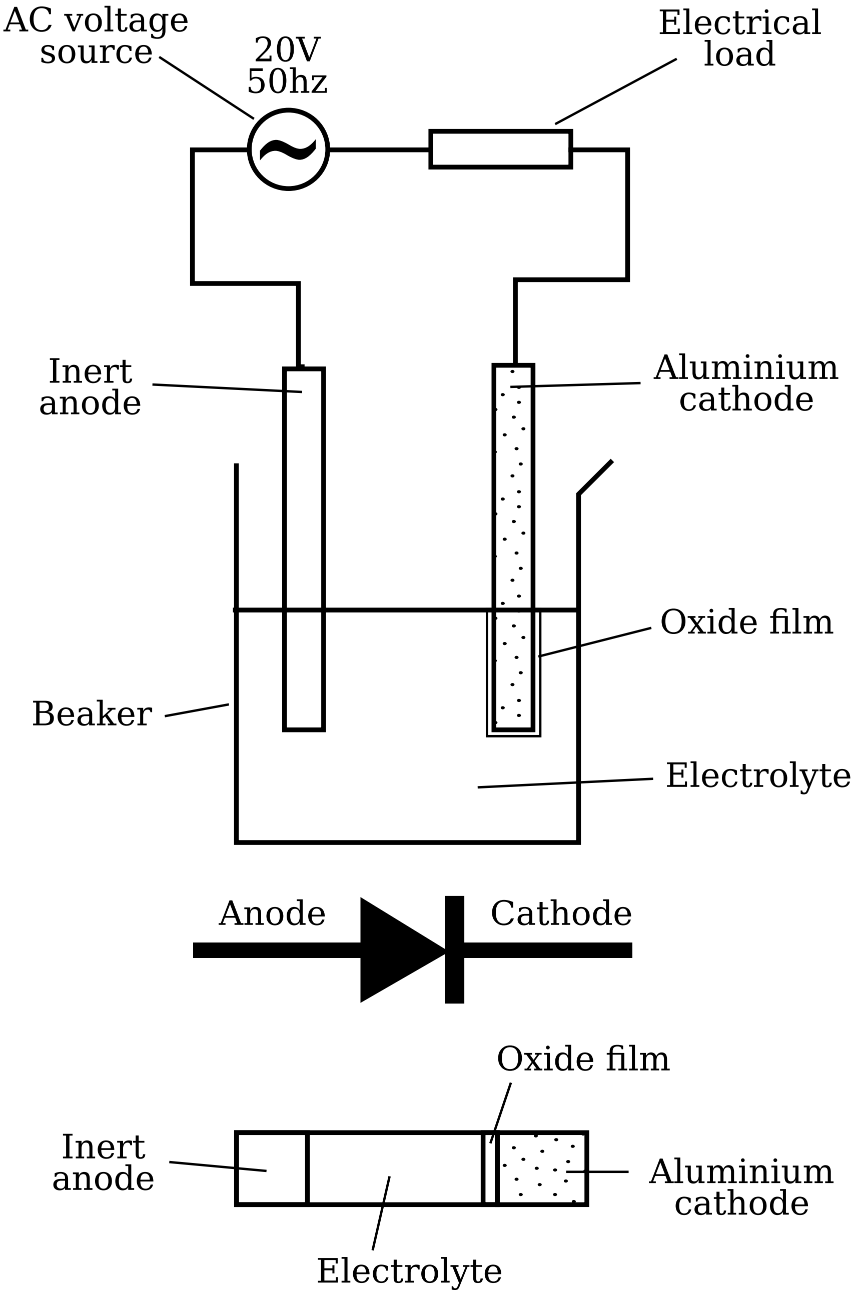

Figure 11: Top: aluminium electrolytic rectifier supplying rectified current to a load. Bottom: equivalent device constructed linearly.

During forward rectifier operation the insulating layer dissolves either partially or completely (Fitch 1926), depending on the insulator forming conditions and time the rectifier has spent since last being reverse biased. The electrolytic rectifier then continues to conduct.

AERs share similar chemistry to aluminium electrolytic capacitors, however literature on electrolytic capacitors is difficult to use for studying AERs. A small electrolytic capacitor charges up quickly and then blocks current if used in one direction, but then discharges and "fails" short if used in the opposite direction, just as an AER does. Unfortunately aluminium electrolytic capacitor related research is difficult to obtain, leading to a perception the industry may keep much of their research confidential.

4.1.2 Materials

A variety of materials can be used to construct electrolytic rectifiers with varying performance.

Cathode Whilst the cathode can be made of aluminium, magnesium, tantalum or any other metal that forms an insulating oxide (Fitch 1926); the most commonly used and tested material in literature is aluminium; likely due to its ease of access. Nickel cathodes have the special property of changing colour when an insulating oxide layer is grown during rectifier operation (Heffner 2006).

Anode The anode must be made of a chemical that is conductive but does not react with the electrolyte. Common options include (Kruse 1922, Atkinson 1921):

- Lead
- Steel
- Carbon (graphite)

Heffner (2006) contentiously claims that the anode can be made of the same material as the cathode (eg aluminium-aluminium) or of a different material normally used to make the cathode (eg aluminium-magnesium) provided a differential build-up of insulating layers is achieved. No other sources confirm this, and others (Steiner 2003) use such symmetric systems to demonstrate devices that intentionally do not operate as rectifiers.

Electrolyte Many sources suggest the use of disodium tetraborate $Na_2B_4O_7$ (“Borax”) or sodium hydrogen carbonate $NaHCO_3$ (“Soda Bicarb”) dissolved in water as an electrolyte, likely due to the easy access to these materials. Fitch (1926) also claims that Borax electrolytes provide higher performance than most other electrolytes.

Sources list a wider variety of electrolytes with varying performance levels:

- CaO Calcium oxide (“Pickling Lime”) (Heffner 2006)
- CH_3COOH Ethanoic acid (“Acetic Acid”) (Heffner 2006)
- $C_3H_4OH[CO_2NH_4]_2$ Ammonium citrate (Fitch 1926)
- KCN Potassium cyanate (Fitch 1926)
- $KMnO_4$ Potassium permanganate (Fitch 1926)
- NaH_2PO_4 Sodium phosphate (Kruse 1922)
- Na_2SO_4 Sodium sulphate (Fitch 1926)
- Na_2SiO_3 Sodium metasilicate (“Water glass”) (Heffner 2006, Fitch 1926)
- $[NH_4]_2CrO_4$ Ammonium chromate (Fitch 1926)
- NH_4HCO_3 Ammonium bicarbonate (Fitch 1926)
- NH_4HPO_4 Ammonium phosphate (Fitch 1926, Kruse 1922)

The exact chemical requirements for an electrolyte to work in an electrolytic rectifier are unknown. Whilst many of these compounds dissolve into carbonate, phosphate or sulphate ions in water; notable exceptions such as borax exist. Previous research has focused on identifying which electrolytes work in practice and quantifying which electrolytes work best, rather than investigating the actual chemical processes involved.

Whilst information on modern aluminium electrolytic capacitor chemistries is difficult to obtain, anecdotal electronic industry knowledge suggests they base their electrolytes on compounds using Borax.

Electrolyte Additives Various additives are recommended by different authors and industries:

- Electrolytic capacitor sources typically suggest ethylene glycol based additives to prevent freezing.

- Kruse (1922) recommends ammonia for unspecified performance purposes.
- Fitch (1926) recommends a gelling agent for unknown purposes.

In general the literature reviewed poorly defines the cases for these additives and they appear to be non-essential.

4.1.3 Optimisation

The performance of an electrolytic rectifier is controlled by four factors:

1. Purity of the ingredients
2. Choice of electrolyte
3. Operating temperature
4. Surface area of the electrodes
5. Forming process employed

The purity of the aluminium electrode is important for rectifier life (Kruse 1922, Fitch 1926). Sources from the 1920's go into great detail suggesting where the correct types of aluminium can be sourced to avoid additives and impurities. Poor purity can sometimes be observed as uneven glow on the cathode (Kruse 1922) and later through "poisoning" (discolouration) of the electrolyte or plates (Kruse 1922, Atkinson 1921).

Some sources demand that distilled water should be used to prevent early device failure (Kruse 1922) whilst others suggest that devices be tested (through the forming process) and cleaned out if they fail. In contrast no discussion exists over the purity of compounds dissolved into the water to form the electrolytes.

Every source quotes different figures for the maximum reverse voltage each aluminium electrolytic rectifier can sustain. Fitch 1926 attempts to explain this through tests across a variety of different electrolytes that show vastly differing performances, with compounds such as sodium sulphate only being able to sustain reverse voltages of up to 40V and borax surviving voltages of almost 500V. Kruse 1922 instead tries to explain this variance through the different operational modes of an aluminium electrolytic rectifier ("overloaded" or not, see section 4.1.4), the purity of ingredients used and a user-chosen trade-off between performance and lifetime. Overall there is no consensus on exactly what voltage rating to apply to aluminium electrolytic rectifiers, other than it lives in the 40V to 500V range.

Aluminium electrolytic rectifiers should not be operated far above room temperature (Atkinson 1921, Kruse 1922) in order to avoid rectifier damage.

4.1.4 Operating modes and surface theory

Aluminium electrolytic rectifiers are described to have either small sparks (“fireworks”) or a dull blue-green glow on the aluminium electrodes during operation.

Fitch (1926) and Atkinson (1921) describe these sparks as normal parts of the operation of the rectifier, however Kruse (1922) disagrees and claims they are an incorrect form of operation that leads to faster device degeneration. Kruse further claims that the absence of or pattern of cathodic glow can be used to diagnose whether or not a rectifier is “healthy”. Kruse claims there are two operational modes of AER:

- Correctly loaded, with the aluminium electrode “glowing” evenly.
- Over-loaded, with the aluminium electrode exhibiting small “fireworks” or uneven glow.

Over-loading can be solved through several methods:

- Increasing the surface area of the plates in the solution, so less current density (current per square area) exists.
- Reducing the reverse voltage each AER needs to block (by inserting more AERs in series).
- Cleaning and remaking the AER with fresh ingredients.
- Using purer aluminium cathodes.

4.1.5 Capacitance

All diodes have capacitance and it is typically desirable to minimise this capacitance so the diodes can be used at high frequencies. AERs have traditionally been used in low-frequency (50-60Hz) applications and Fitch (1926) claims that they can operate up to approximately 1kHz.

The capacitance of an AER is dependent on the surface-area and spacing of the electrodes, as in traditional capacitors. Unusually it is also heavily dependent on the voltage applied (Fitch 1926), reducing rapidly as the voltage is increased.

4.1.6 Forming

Whilst the insulating layer on the cathode is instantaneously developed if a reverse potential is applied to a freshly constructed AER, the performance and reliability of the device is increased if the layer is initially "formed" before use over a longer time period. A wide variety of forming conditions and their outcomes are documented by different authors.

Forming appears to be electrically analogous to the charging of a capacitor, which is not coincidental considering the similar chemistry between an AER and an aluminium electrolytic capacitor. During the insulation forming process a current "leaks" through the device. As the layer forms this current reduces. Raising the voltage across the device then temporarily increases the current draw in a similar fashion until the insulating layer is further developed.

Atkinson (1921) suggests a high current forming process where the secondary of a transformer is placed directly across the AERs. The author admits that many AERs fail this forming step, developing "black scabs" on the surface of their cathodes and failing to perform rectification duties. It appears that this "uncontrolled" forming method also requires a long period of time (a few hours) to complete.

Kruse (1922) instead suggests the use of series resistances and gradual voltage increases to limit the forming currents. Kruse claims that this forming process can be completed in as little as 60 seconds, likely due to the controlled application of power allowing higher voltages to be applied without risking high-currents. Similar to Atkinson, Kruse notes that some devices fail this initial step.

4.2 (Part A) Theory of chemical operation

4.2.1 Limited literature

Very little chemical reaction information is available from electrolytic rectifier sources. Aluminium electrolytic capacitors, devices which have extremely physical and chemical similarity to AERs, would be expected to have greater literature available on their internal chemical reactions; however information in this area is also similarly lacking.

The formation of aluminium oxide on the aluminium plate of aluminium electrolytic capacitors is typically described using two equations (P. Wright):

1. $2\,\mathrm{Al(s)} + 6\,\mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{Al(OH)_3(s)} + 3\,\mathrm{H_2(g)}$
2. $2\,\mathrm{Al(OH)_3(s)} \longrightarrow 2\,\mathrm{AlO(OH)\,(s)} + 2\,\mathrm{H_2O\,(l)} \longrightarrow \mathrm{Al_2O_3(s)} + 3\,\mathrm{H_2O\,(l)}$

The first equation describes the development of aluminium hydroxide, a step that releases hydrogen gas. This behaviour is generally unwanted in both electrolytic capacitors and AERs as it “drys” out their electrolyte; however it only occurs in quantity under certain conditions (such as initial forming or device overload).

The second equation describes the conversion of aluminium hydroxide into the final aluminium oxide layer. This equation does not describe the creation of any gases.

These equations do not align with observations made during actual experiments where gases bubble from both electrodes, not just the aluminium cathode (example figure 41). To resolve this more detailed chemical equations are theorised in section 4.2.3.

4.2.2 (Part A) Experimentation with the pH and air sensitivity of AERs

AER devices operated with widely varying properties during initial experiment attempts:

- Some batches of devices would immediately fail short (conduct in both directions instead of only one).
- Some batches of devices would temporarily operate and then fail short a few minutes later.
- Each device had a unique forward impedance and unique backward impedance, only partially correlated to its batch and electrolytic surface area.

Two theories were developed to try and explain these phenomena:

1. Purity of the water used.
2. Exposure of mixed electrolytes to air for extended periods (whilst stored in bulk in an open container such as a beaker or drinking glass).

Full experimental method, results and discussion are in appendix item 11.1.

Conclusions: AERs interact heavily with the atmosphere, typically becoming “higher quality” (more reliably, less leakage) if their electrolyte is left exposed to air for at least a few hours.

4.2.3 Resulting theorised operation

When sodium bicarbonate is dissolved into water an (initially) alkaline solution forms:

(1) $\mathrm{NaHCO_3(s)} \longleftrightarrow \mathrm{Na^+(aq)} + \mathrm{HCO_3{}^-(aq)}$

Atmospheric carbon then slowly dissolves into the solution, creating carbonic acid:

(2) $\mathrm{CO_2(g)} + \mathrm{H_2O\,(l)} \longleftrightarrow \mathrm{H_2CO_3(aq)}$

Equations (1) and (2) are incomplete conversions. The resulting acids and bases interact in the same solution. This creates a self-stabilising buffer. Both reactions can provide $\mathrm{HCO_3{}^-}$ ions.

When aluminium is introduced into the system and potential is applied the formation of aluminium oxide can be described as:

(3) $4\,\mathrm{Al_3{}^+(s)} + 6\,\mathrm{HCO_3{}^-(aq)} \longrightarrow 2\,\mathrm{Al_2O_3(s)} + 3\,\mathrm{H_2(g)} + 6\,\mathrm{CO_2(g)}$

This notably shows gases being formed. In practice these gases can be observed developing as small bubbles on the surfaces of electrodes during AER testing, an example of is shown in figure 41.

4.3 (Prior research) Applying AERs to make digital logic ICs

Background Whilst AERs have been historically demonstrated for power rectification, they had never been used in the context of PCBs, ICs or digital logic.

Aim To develop an extremely simple and reliable method of “laying down” ionic diodes onto PCBs and other common materials; to verify that these devices operate as diodes and determine if they can be used for digital logic operations.

Results

- AERs function as diodes at low (<100Hz) frequencies (see figure 13)
- AERs can be made very simply and on a very small scale (see figure 12).
- AERs can be arranged into grid to form primitive forms of digital logic, in the form of “lookup tables” (see figure 14).

(Hales 2017, part3)

Figure 12: A single ionic diode (AER) composed of a cupronickel coin (inert anode), sodium bicarbonate in water (electrolyte) and aluminium foil (cathode) assembled on a piece of tape.

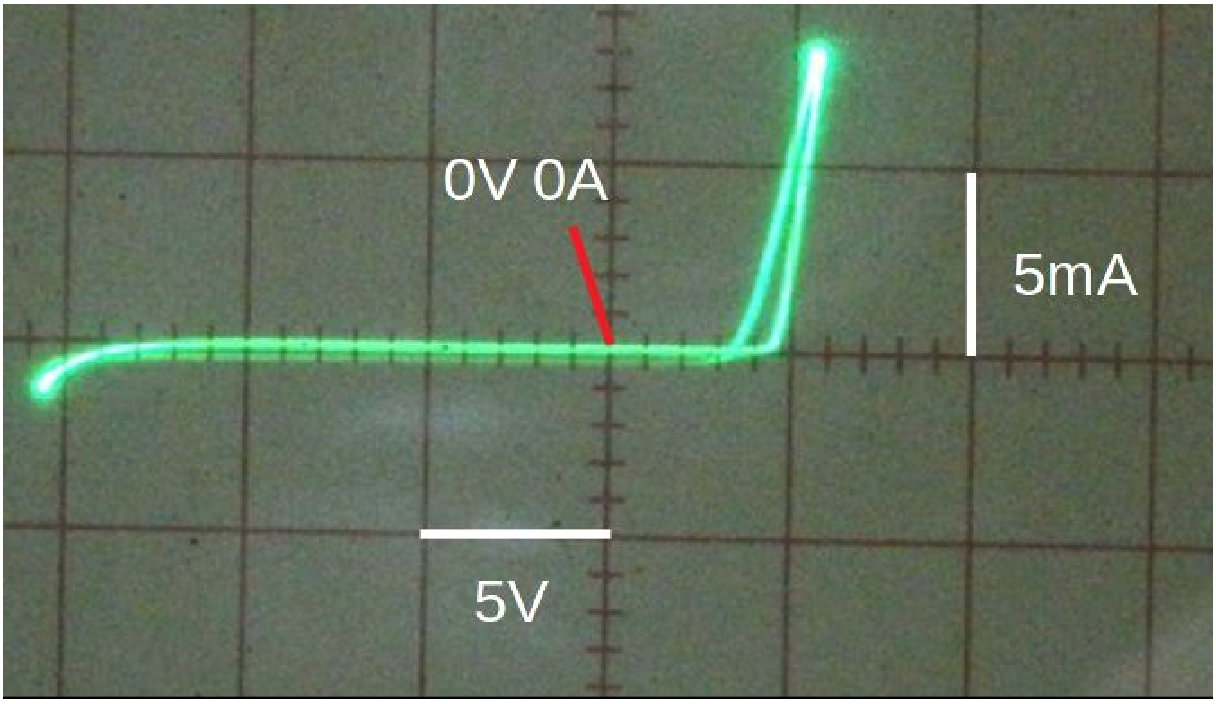

Figure 13: Current versus Voltage graph of the device shown in figure 12, demonstrating its diode-like behavior. A full explanation of diode curves is given in Thesis A (Hales 2018).

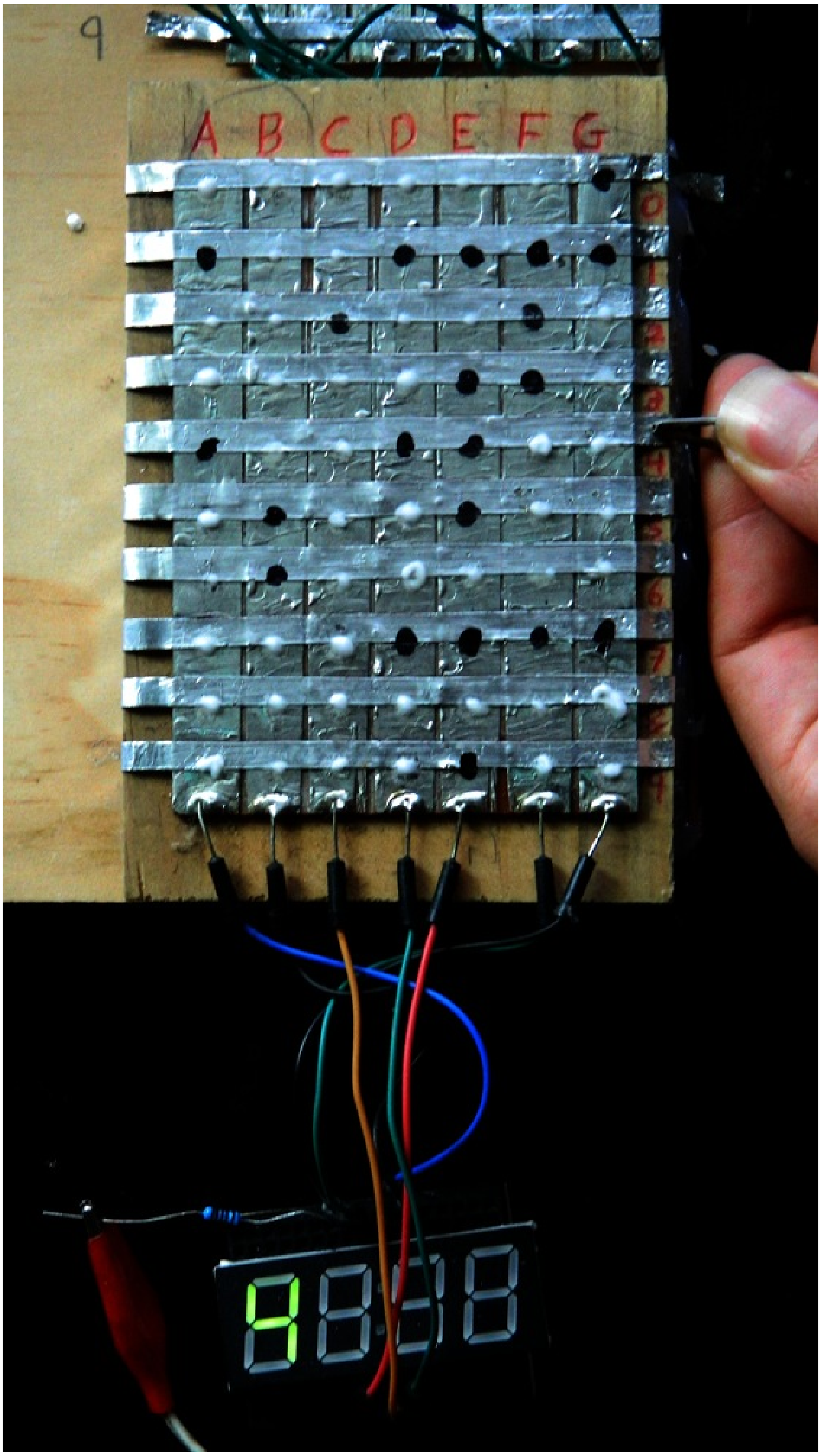

Figure 14: An array of ionic diodes (top) acting as a lookup-table to operate a seven-segment display (bottom). The number '4' is being displayed as the fourth row of the matrix has a signal applied to it. White dots represent deposits of electrolyte and black dots are inert permanent marker. Horizontal aluminium strips form cathodes and vertical tin-coated copper strips form anodes.

Discussion and Conclusions The results of this research proved that ionic diodes were practical enough to be used for basic electronic operations and suggested the feasibility of ionic devices for this thesis.

Notably the application of AER diodes in the form of 'lookup tables' (figure 14) provides some ability to perform digital logic, however without working useful amplifiers/transistors (to implement encoders and decoders) this logic family is very limited.

4.3.1 Other notable AER behaviours

- AERs can only operate whilst the electrolyte is wet. Electrolyte deposits on PCBs typically dry in less than 15 minutes, with device operation reducing over this time.
- AERs can be "re-wet" to immediately restart their operation. Re-wetting is best done using a pre-mixed solution of electrolyte.
- AERs operate even with excess electrolyte solids inside of them, however the effects this has on performance have not been studied.
- The turn-on voltage for an AER is approximately 5V, see figure 13.
- The reverse-breakdown voltage of an AER increases the more the device is used and formed.

4.4 Electrolyte concentration limits

Initial experiments in part A used saturated solutions of NaHCO3. Some part B experiments, such as concentration control devices (section 6.4), require lower concentrations of solution to operate.

Aim To determine the lower limit of $NaHCO_3$concentration required for AER devices to continue operating.

Method

1. Start with a 0.01 molar solution of sodium bicarbonate (119g water to 0.1g of NaHCO3[9]).
2. Create further diluted mixes in 10:1 ratios

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[9] Calculated using the molar mass of NaHCO3, as per standardard chemistry methods. As NaHCO3 absorbs atmospheric water this method is only approximate.

3. Test if each of these mixes can create an AER with a defined 5V turn-on point.
4. Compare impedance of these devices to plain de-ionised water.

Results and discussion At 0.0001 molar concentration a weak 5V turn-on is still observed. Below this the turn-on point is poorly defined and the device impedance are similar to that of plain DI water.

Whilst plain DI water should (theoretically) have a very high impedance, it proves difficult to clean all residues off testing apparatus between each trial. This problem is similarly faced

0.01 molar is a "useful" concentration that provides impedances similar to saturated mixes without creating solid white NahCO3 deposits as readily whilst drying. These deposits can interfere with device operation (see section 7.4).

The surface-area of the aluminium contact is a variable that was not controlled in this experiment. It was assumed that this would be unimportant provided constructed devices use aluminium surface areas within the same order of magnitude as this test, however this assumption is challenged in section 6.4.2. Future experiments should control this variable.

5 Transistor proofs: methodology and misdirection

The next major sections of this report describe experiments attempting to create and verify transistors. Before moving onto these topics it is necessary to first identify and recognise what qualities are expected from a transistor.

Many works of literature claim to describe devices with transistor-like action but do not provide the necessary or correct substantiating proof. It appears that many researchers do not understand what a "useful transistor" is in an electrical context.

In this section prior transistor descriptions and proofs are challenged and a simple method of proving that a device is a "useful transistor" is put forward.

5.1 Lexigraphical difficulties: defining "transistor"

This thesis aims to develop an IC technology containing transistors, so it is important to first understand what a "transistor" is. This is surprisingly difficult, with many definitions conflicting or fundamentally incompatible with the goals of this thesis.

For this thesis a "definition by purpose" method is considered to be the most appropriate.

5.1.1 Defining by example: limitations of experiences

Definitions of "transistor" vary heavily depending on the perspectives and experiences of the author of the definition.

- AHD (2019) describes a transistor as requiring at least three electrical contacts and Howe (1995) demands a transistor be a three-terminal device.
- Howe (1995) goes further and declares that there are only two "kinds" of transistor, bipolar and field-effect.

These definitions are likely born from the limited perspectives and experiences of the engineering industries their authors come from.

In practice almost all off-the-shelf transistors are three-terminal devices, so in the areas of electronics design and manufacturing it is not unusual to consider transistors as only three-terminal devices. It is likely that AHD (2019) and Howe (1995)'s definitions are from these backgrounds. In reality four-terminal transistors are not uncommon in items such as bidirectional transmission gates and two-terminal transistors are arguably possible in the form of resonant tunneling diode amplifiers (see section 8.2). Fundamentally these definitions are wrong, but for certain practical purposes they are "correct enough".

Similarly the computing-focused background of Howe 1995 (published by the Free On-Line Dictionary of Computing) would likely limit that author's experience to the families of transistor traditionally used to manufacture central processing units (CPUs). Whilst dozens of transistor families exist beyond bipolar and field-effect devices, Howe's two-family definition is "good enough" for modern computing history purposes.

None of these "definitions by example" provide an appropriate definition of "transistor" for this thesis, as they are too restrictive and potentially exclude solutions that provide the same functionality as traditional transistors but use different operational methods to do so.

5.1.2 Changing meaning: etymology versus current usage

It is worthwhile understanding how context and the definitions of words have changed when interpreting older texts discussing transistors, such as Letaw and Bardeen (1954) (see section 5.7.1). The modern definitions of "transistor" or the definitions that are useful for the purposes of this thesis do not necessarily align with the original usage of the word.

The word "transistor" is believed to be a combination of "transfer" and "resistor" (Harper 2019, Augenbraun et al 1999). Notably this definition does not imply that the a transistor must amplify. Any form of modulatable resistor potentially matches this meaning.

The strictness of meaning to the word "transistor" in historical contexts is low, with some sources (Augenbraun et al 1999) claiming that it was coined merely as a marketing term.

In more modern texts a definition based on purpose or example is typically used instead of etymological or marketing roots.

5.1.3 Defining by purpose: limitations of ambiguity

Some sources combat this over-specificity by "defining by purpose" instead of "defining by example":

- Riordan (2018) and Wordnet (2019) only require that a device is semi-conducting and can amplify, nothing more.
- AHD (2019) initially provides a restrictive definition-by-example, but then widens it with "Any of various devices serving the same purpose but employing a different technology".

From these definitions it could be concluded that *any amplifying device that modulates its resistivity* (ie a semiconductor) is a transistor. This is a wide definition more suitable for the functionality-driven goals of this thesis, as it allows any device that provides similar functionality to a traditional transistor to be considered a success. Two notable points of contention are however raised:

1. Historical counter-examples, such as vacuum tubes.
2. What does it mean to "amplify"?

Vacuum-tubes are traditionally not considered to be transistors, as transistors were historically the devices that replaced vacuum tubes (in most designs). A vacuum tube such as a triode or pentode does however provide equivalent functionality to a transistor and its low-pressure contents could still be considered to be a gaseous/plasma form of semiconductor, so for the "define by purpose" method of this thesis it could be considered a type of transistor. The historical and cultural motivations of separating the definitions of "transistor" and "vacuum tube" have no meaningful impact on the research goals of thesis, so historical counter-examples such as this can be ignored.

Amplification is a more complex topic. In the sections ahead it is shown that devices that appear to "amplify" or have gain can still be completely useless for the purposes that transistors are normally used for.

5.1.4 Sidenote: "amplifier" versus "transistor"

A transistor is the active (non-passive) component of an amplifier. Amplifiers typically require multiple components (including resistors) to function, but is possible to operate certain typologies without under certain circumstances.

It follows that a "useful transistor" is the active component of a "useful amplifier". Throughout this paper the distinction is of little consequence as all devices demonstrated aim to show both useful transistors and useful amplifiers simultaneously.

5.2 Amplification is not enough: easily misleading gain interpretations

There are many ways that a researcher can incorrectly conclude they have created a transistor-like device. One particular method is misinterpreting circuit measurements to claim that gain exists when it does not. This particular problem was encountered during experimentation with an aluminium-electrolytic transistor prototype in section 6.3.1.

Take the example circuit shown in figure 15, where a three-terminal device is being tested to see if it is a transistor. The input V & I are swept and the resulting V & I in the

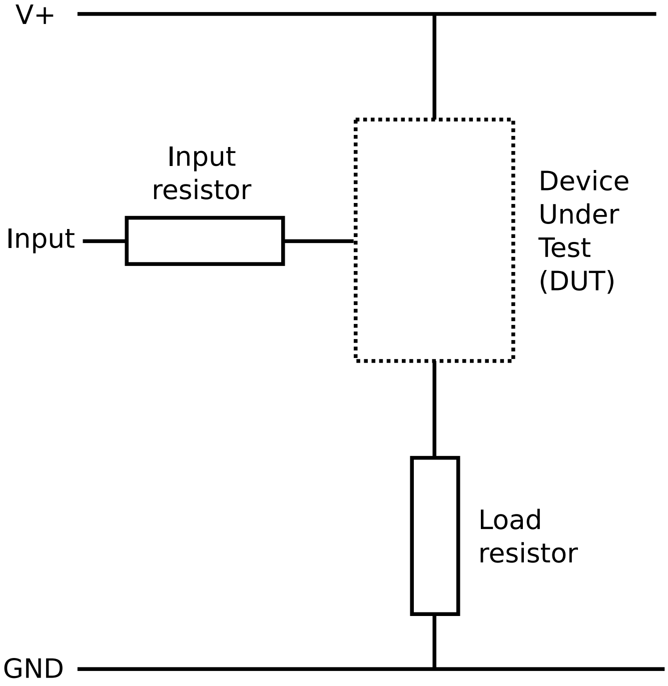

Figure 15: Example circuit for testing if a three-terminal device could be a transistor. Depending on this nature of the DUT this circuit may be interpreted as a common-collector or common-emitter amplifier.

load resistor are then measured. An example plot of the input vs output currents for this circuit are in figure 16.

Between 5-10V of input voltage it appears that this device exhibits current gain. ie the output current is larger than the input current.

$$\text{Equation 1: } Current\,gain = \frac{Output\,current}{Input\,current}$$

From the outset it appears that this device both semiconducts (changes resistance) and amplifies, meeting some definitions of a transistor.

Unfortunately the interpretation of this graph to show amplification is completely artificial. “Gain” is a synthetic concept and in this case the gain being shown *cannot* be used to amplify or buffer signals, meaning that this device is not a *useful* transistor or amplifier.

The next paragraphs describe ways of proving this.

Counter-model Consider that the DUT from the previous example is a simple resistor divider, as shown in figure 17. This circuit would (with the correct real resistance values) provide results identical to those shown in figure 16.

A device made of only resistors cannot amplify or buffer a signal to a load. It is not considered a transistor (let alone a useful transistor) at all. It can only *attenuate* a signal.

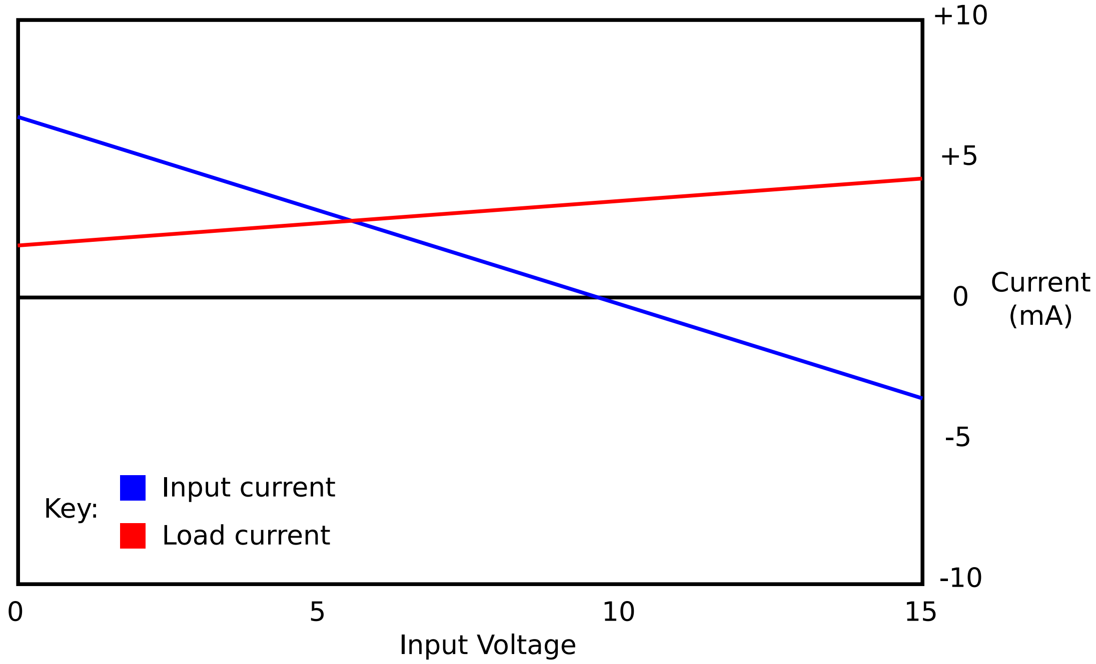

Figure 16: Current transfer characteristics for the circuit in figure 15 after a voltage sweep is applied to the input terminal. For report brevity the counterpart voltage transfer characteristics are omitted, however they should be analysed in a similar fashion.

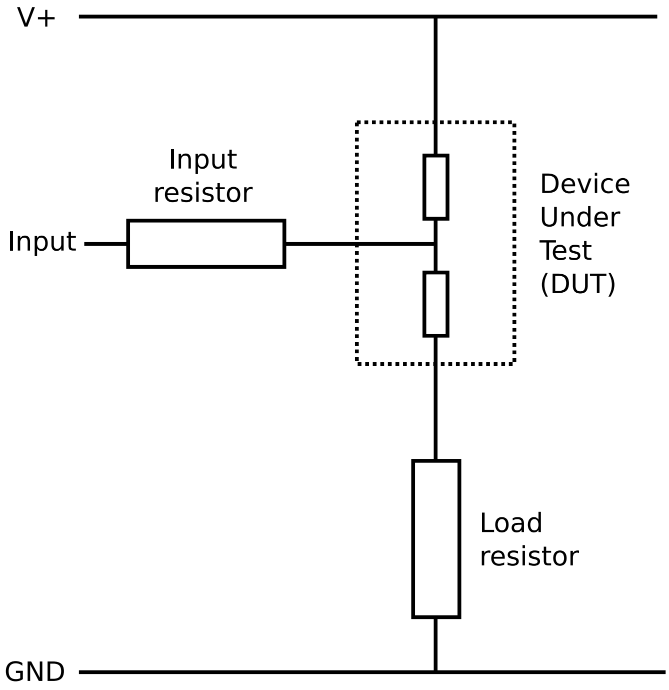

Figure 17: Resistor-divider counter-model.

It is important to note that the resistors in the divider could be non-linear (creating curved rather than the straight current responses shown in figure 16) and the circuit would still not amplify. A real-life example of this is graphed and documented in section 6.3.1. This can be modeled in simulations by adding non-linear and non-amplifying devices such as diodes into the voltage-divider DUT.

Simulating signals in and out of the device

1. Choose an input signal that sits inside the range the device is supposed to amplify over.
   Eg: let the input signal be a sinewave traveling from a minimum of 5V to a maximum of 10V.

2. Read the graph in figure 16 to determine what range of input currents this will result in.
   Answer: 3 to 0 mA

3. Read the graph in figure 16 to determine what range of output currents this will result in.
   Answer: 3 to 4mA

The original signal of peak-to-peak amplitude 3mA has been reduced to a peak-to-peak amplitude of 1mA. The device has attenuated, not amplified. It has also DC-shifted the signal, but this is again not amplification (as it can equivalently be achieved by adding a DC supply in series with a signal, something that does not make the signal "bigger").

Importantly a similar analysis should also be performed to the voltage-transfer characteristics to determine if there is any voltage-to-voltage gain. In this particular example this process has been omitted for brevity, however if the counter-model in figure 17 is considered then similarly attenuating results will be obtained.

Impossibly high gain The current curves in figure 16 show the input current approaching zero as the input voltage approaches 10V.

If we calculate the current gain as per equation 1 then at 10V our gain approaches infinity. This is not physically possible.

Methods of analysis should always be heavily questioned when their application results in impossible quantities.

5.3 Impedance modulation is not enough: proven fanout is required

A device that can change its impedance can be considered a transistor, but it is not necessarily a "useful" transistor as it may not provide the ability to "fanout". To provide fanout a device must be able to amplify the power of a signal by more than a factor of 1.0, preferably much more.

If a device can only attenuate then it can only be used to make overall systems of very short "length". Take for example a simplified view of fetching information over the internet:

- A server contains data that someone wants.
- A copy of this data is sent from the CPU to an ethernet interface chipset.
- This ethernet chip amplifies the message into ethernet driving levels.
- Every switch and router along the way takes an attenuated ethernet signal (due to line impedances) and re-amplifies it back to specification again.
- A final receiving computer amplifies this signal into (amongst other forms) the voltage levels needed to drive pixels on a display.

If each amplifier along this chain can only attenuate signals then the server would have to expend very large amounts of power to ensure a signal of usable amplitude reaches the receiving screen on the receiving computer on the other side of the internet.

Additionally: two way communication and feedback loops are mostly impossible if only attenuating transistors are available. Some circuits would still be possible, but in very limited and non-modular forms.

5.4 Non-linearity is not related transistor action

A non-linear device is not certain to be a transistor, and a device that shows linear current-versus-voltage (IV) characteristics can still be a transistor. Examples:

- A JFET has a very large linear (ohmic) region of operation in its drain-source IV curve, but it is still a transistor capable of amplification (including in this region of operation). See figure 18.
- A diode provides very non-linear IV curves (see figure 19), but it is not considered a transistor or an amplifier.[10]

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[10] Technically a diode can function as an amplifier (see tunnel diode logic in section 8.2), however this behavior is not shown in the figure/curve denoted.

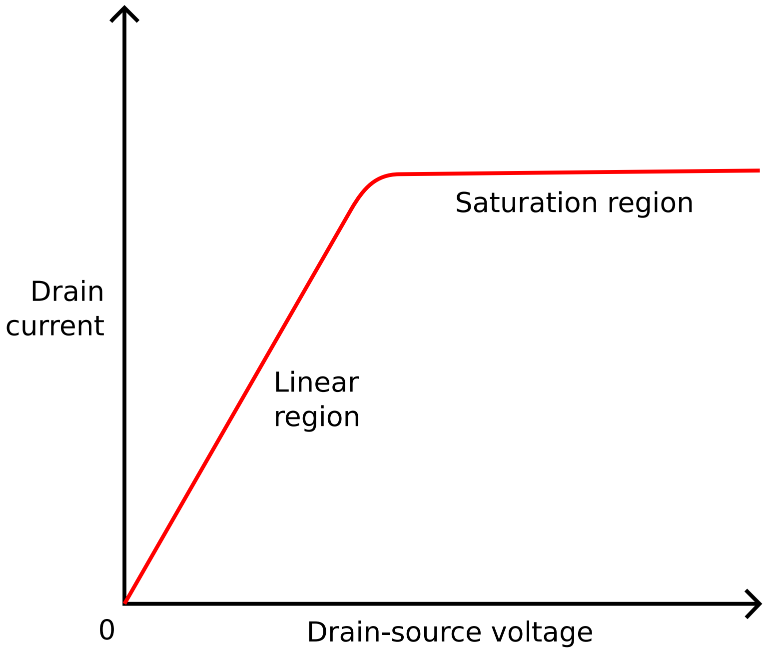

Figure 18: Relationship between channel current and channel (drain-source) voltage for a JFET when it is held under a constant bias (Vgs) condition. (Linear systems 2014)

Additionally: all device show non-linear behaviour if voltages or currents large enough are applied to them. Non-linearity is not a special or unique property.

5.5 Turing complete logic: signal inversion

We take for granted that traditional transistors can be used to create both inverting and non-inverting amplifiers. Inverting amplifiers, combined with diodes, create a family of logic called "diode-transistor logic" (DTL) that is Turing-complete.

Whilst there are many other logic families that describe ways that transistors can be used to achieve Turing-complete logic: the vast majority of them require (or assume) the ability to create inverting amplifiers.

If a potential transistor technology cannot be used to create an inverting amplifier: it should *not* be assumed that it can be used to create Turing-complete circuits *unless* specific (unique) methods of doing so are found and demonstrated.

For example: if a transistor can only be used in "follower" style amplifier arrangements then it cannot invert signals and therefore cannot be used to implement all types of logic gate. Unless this transistor has other special and unique properties that allow it to be used to create turing-complete logic (eg non-linear tunnelling, see section 8.2) it is unlikely to be a "useful" transistor.

Achieving "Turing completeness" is complex (and even unexpected) under many circum-

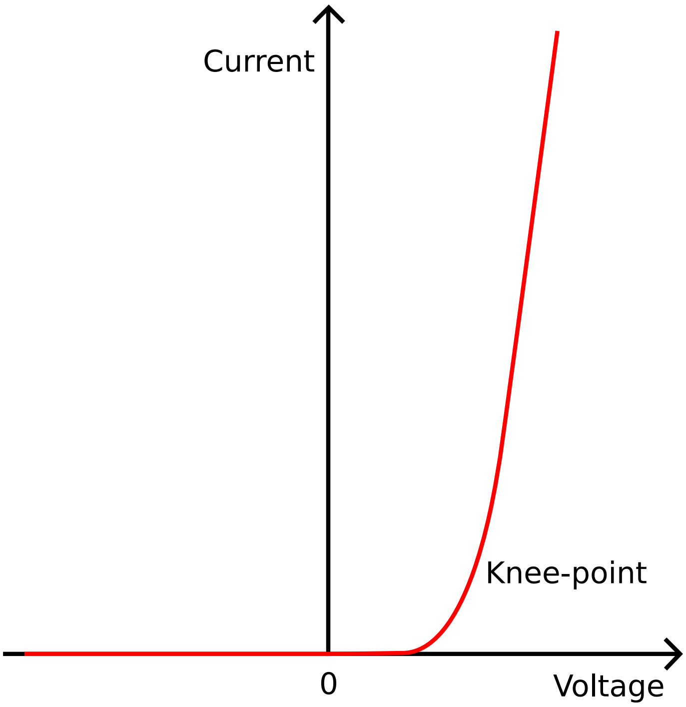

Figure 19: Relationship between current and voltage for a normal transistor, under common operating conditions.

stances, so this requirement is not included in the simplified practical tests written in the following subsection. This topic should only be considered if a transistor family with unusual restrictions (ie inability to create common emitter/collector amplifiers) is encountered.

5.6 Test-based practical definition of a "useful amplifier"

A definition based on the ability for a transistor to "amplify a signal" is very concise, but it does not present a clear methodology of how to test and prove this quality. The following tests are provided as a practical alternative.

To prove a device is a "useful amplifier" it must, for at least one chosen operational region (range of inputs), pass all of the following tests simultaneously:

Test 1 One output parameter (voltage, current or power) must change more rapidly than the *same* parameter at the input. [11]

Test 2 A power gain greater than 1 is obtained.[12]

---

[11] Voltage-to-current gain and current-to-voltage gain are difficult to directly compare for this test, see section 5.6.3.

[12] Rule 2 notably excludes transformers from being considered as useful amplifiers. Without power-gain you cannot cascade transistors to form complex circuits.

Test 3 The device exhibits stable behavior, ie the device can meet points (1) and (2) continuously.[13]

These requirements are not exhaustive, however a device that does *not* meet them is *definitively not* a useful amplifier.

A device that does not meet these requirements can still be useful as part of a larger circuit (containing useful amplifiers in other forms), but alone it cannot be considered userful or turing-complete.

Example synthetic test results for potential amplifiers are shown and debated in figure 20

5.6.1 Biasing and drive arrangements

Devices that require bias into a certain region of operation (such as item *(iii)* in figure 20) place certain restrictions on their use. This is not unusual: most traditional transistors also have bias requirements, with more complex amplifier arrangements (eg op-amps) existing to try and counter-act but (often) not completely remove this problem.

Restrictions of needing bias include:

1. Requiring inconveniently large power supplies (relative to output range). Eg: a 3 to 5V output may require a 0 to 12V power supply.
2. Providing inconveniently small linear operation regions. If the "useful" amplification region is non-linear then an even *smaller* semi-linear within this must be chosen if linear analog (non-digital) operation is required.
3. Requiring split-rail power supplies if DC offsets in the output or input are not permitted and the signals cannot be AC-coupled.

5.6.2 The Difference between test (1) and two-port network parameters

Two-port networks are only defined for linear systems. A non-linear amplifier can still be considered a useful amplifier.

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[13] DC is not required, a device that can only amplify AC on a continuous basis can still be considered stable and useful. This third rule negates energy-storing devices (such as capacitors) from being considered as useful transistors.

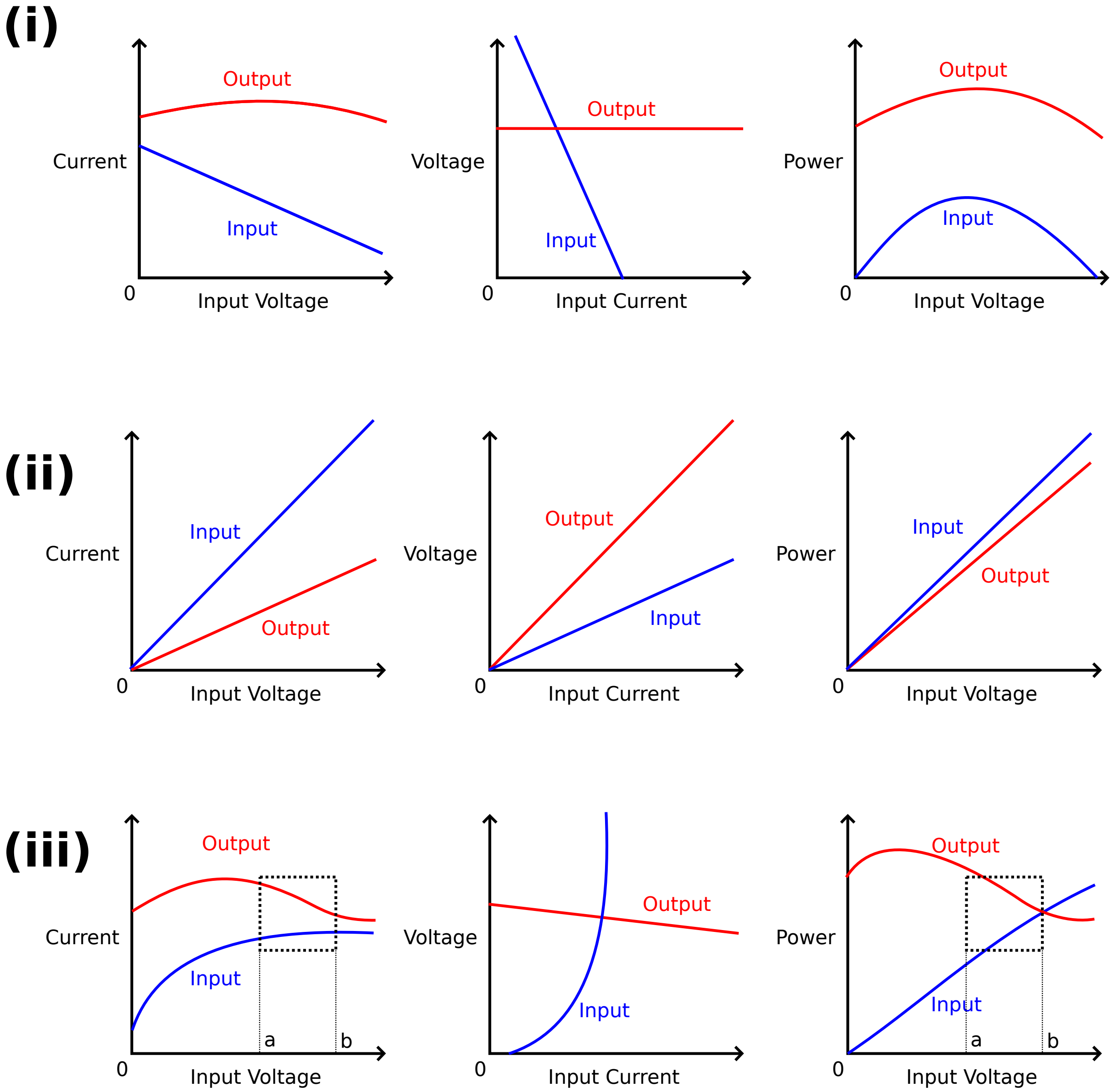

Figure 20: Measured and calculated transfer characteristics of several (synthetic) amplifier attempts.

Device (i) meets power gain requirements (test 2) but fails slope requirements (test 1). A signal at the input will be replicated at the output in an attenuated form.

Device (ii) meets slope requirements for input vs output voltage (test 1), but fails power gain requirements (test 2). This device is likely a transformer.

Device (iii) meets both tests (1) and (2) in the selected region. This device can be used as a useful amplifier when biased to operate in this region.

5.6.3 Transimpedence amplifiers and test (1)

Transimpedence amplifiers take an input current and amplify it into an output voltage; or visa versa. It is undefined whether or not a signal has been amplified when the units for measuring input and output differ.

Transimpedence amplifiers are not considered in this thesis, however two workaround methods for measuring these against Test (1) are suggested for completeness:

1. Consider the output load to be a resistor, a device with known V and I relationship. This allows the output units to be converted.
2. Cascade two opposite conversion (ie V->I and I->V) transimpedence amplifiers in series and consider them as a single device.

A device that cannot complete test (1) using one of these methods it is unlikely to be useful when cascaded with other devices of the same type, meaning it is an attenuator rather than a useful amplifier.

5.7 Example questionable proofs of transistors in literature

5.7.1 Letaw and Bardeen (1954): Electrolytic Analog Transistor

Letaw and Bardeen test devices that appear to be in a common-base amplifier arrangement, where the base is held at a constant voltage and the collector + emitter are used as the inputs and outputs of the amplifier.

Indicative results from some of their tests are reproduced verbatim in figure 21. The 'a' values and lines represent gain ratios [14] where a gain of '1' (unity) is 45 degree line

Unity or below-unity current gain are expected for a common-base amplifier. These types of amplifiers are however expected to provide voltage (and power) gain (Nave 2019).

Letaw and Bardeen do *not* provide any evidence that these devices provide voltage or power gain. Only the input-current to output-current transfer graphs (as per figure 21) are provided, which show attenuation.

No other evidence that directly suggests these devices can amplify small signals into larger ones is provided either.

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[14] This is a different method of plotting input and output parameters to what is shown in figure 20, however this method is just as valid for determining whether or not a device meets the requirements of test (1) in 5.6.

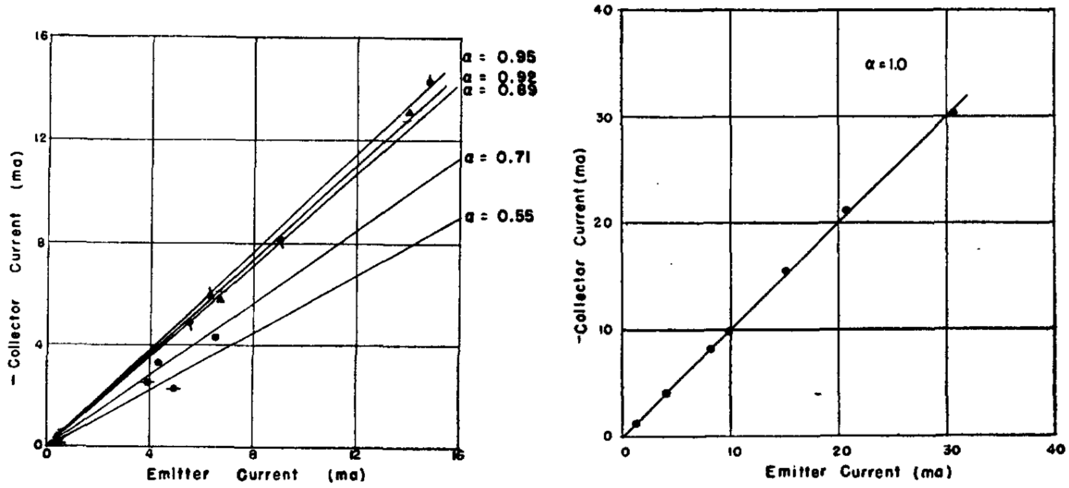

Figure 21: Input vs output current measurements of various devices from Letaw and Bardeen (1954, figures 5 and 8).

There is not enough information to conclude that Letaw and Bardeen's devices are amplifiers. Test (1) of section 5.6 cannot be concluded. Instead Letaw and Bardeen appear to claim the device is a transistor based off its similarity of theoretical ionic methods of operation to the "electrons and holes" operation of solid-state transistors. Inferences based on theories are not valid scientific methods of proof.

Alternatively Letaw and Bardeen may be using one of the older definitions of transistor (an electronically variable resistor) rather than a more modern purpose-driven (amplification) definition. See the lexicographical difficulties in previous section 5.1 for more detail.

5.7.2 Petrenko and Maeno (1987): Ice Field Transistor

Pentrenko and Maeno discuss the surface-conductivity of ice under certain conditions. They claim this device is a transistor, however they do not provide any evidence suggesting that these devices provide useful amplification of signals, nor evidence that could be used to suffice *any* of the tests in section 5.6.

Similar conclusions can be drawn as per Letaw and Bardeen in the previous subsection, however it is worth noting this paper is from a more contemporary context where it is more reasonable to expect that "transistor" means "amplifying device".

6 Aluminium Electrolytic Transistors

The primary route used to try and develop macro-scale low-technology transistors in this thesis has been to adapt the aluminium electrolytic diodes developed and tested in Thesis A (Hales 2018) into a transistor form.

No attempts have been successful so far. These failures have lead to the development of useful testing strategies for future work, such as:

- A four-terminal testing method in section 6.4.3 designed to remove the electrical effects of base-collector and base-emitter junctions in concentration-control devices.
- The test-based transistor proof method in the previous section 5.6.

6.1 Testing apparatus

Transistors to be tested could operate in unknown ways:

- Input behavior similar to FET gates or BJT bases?
- N or P style?
- None of the above?

A circuit was needed that could detect a potentially transistor-like prototype device changing impedance whilst being subjected to a wide range of inputs.

The circuit in figure 22 was developed to solve this problem. Notable features:

- The input voltage to the device can be taken far higher and far lower than the voltages of the device's other two terminals.
- The adjustable DC supply could be wired in reverse, or in reference to the main 12V rail, to extend the input range even further.
- Current and voltage at both the input R_B and the output R_L are easy to measure without the need for in-line current meters.[15]

This testing apparatus is imperfect: traditional transistor modelling also permits the terminals other than the base/gate to be considered inputs under certain circumstances. This apparatus should however at least identify devices that show potential for amplification.

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[15] All DC current meters provide an impedance known as "burden", often this is non-linear due to the input protection circuity. This can bias results in unexpected ways under certain test conditions.

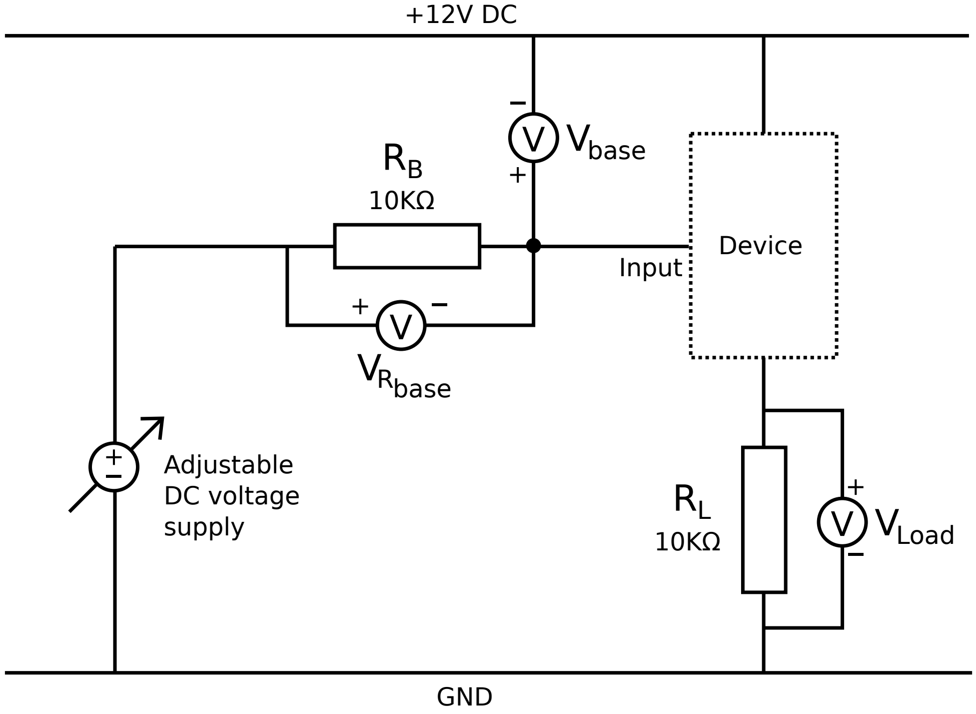

Figure 22: Circuit used to test potential transistor prototypes. Resistor values and ratios were changed experimentally during all tests to try and obtain larger output swing ranges.

6.2 Macro-scale field effect transistors

A feasibility study into the possibility of scaling up FET-style devices to a macro scale was undertaken. It was concluded that the voltages required were impractical, with tests also confirming the devices could not modulate at lower (more practical) voltages.

6.2.1 Insulator thickness and electric field strength

Plain, clear sticky-tape was identified as an easy to access insulator that could be used on the gate of macro-FET style devices, however its thickness was put into question. Actual FET devices rely on extremely thin insulating layers to ensure the electric field can easily penetrate from the gate into the channel.

Measurement method Two aluminium plates where chosen to sandwich the tape between. These plates were sanded flat before use.

Ten layers of sticky tape were sandwiched together between the two aluminium plates. Each layer was individually adhered linearly using a hard object to prevent the formation of air bubbles in the sandwich. The thickness of the aluminium + tape sandwich was measured using vernier calipers and compared to the thickness of the aluminium plates alone.

Results The tested sample of standard clear household tape was 40-43um thick (assumed indicative of all similar tapes).

The tested sample of generic Kapton clone tape was 47-49um thick (assumed indicative of all similar tapes).

Comparison with actual FET insulators Actual FETs typically use 1-10nm gate insulators (Timp et al 2000) and have an “on” gate voltage of around 1 to 10V.

These numbers equate to electric field strengths of 0.1 to 10 gigavolts per meter.

If it is assumed that the need for this electric field strength scales linearly with dimensions, then the ~40um thick sticky tape would require between 400kV and 4kV to obtain the same effects.

These voltages are typically not practical near water and are not conducive to the accessibility goals of this thesis.

6.2.2 (Part A) Experiment: Single-charge ionic FET

A traditional FET was attempted using a channel of sodium bicarbonate electrolyte between two tin (inert) contacts. A conductive gate lay underneath this construction, isolated by a thin layer of polyamide tape, see figure 23.

The small dimensions typically required for near-field effects in a FET were emulated using thin insulating tape (the gate insulator) and by manually aligning the edges of two pieces of copper tape (the drain and the source).

Results The device failed to exhibit any channel modulating effects, maintaining the same level of conductivity throughout all testing, even with the gate being take to +/-30V relative to the drain or the source.

6.2.3 Dual-charge channel theory

Ignoring dimensional & voltage constraints, it is believed this device did not work because of the types of carriers in the electrolyte.

Traditional field effect transistors only have one type of ’free’ charge in the channel, positive or negative, and this charge is manipulated to modify the conductivity of the channel. See figure 2 for an example.

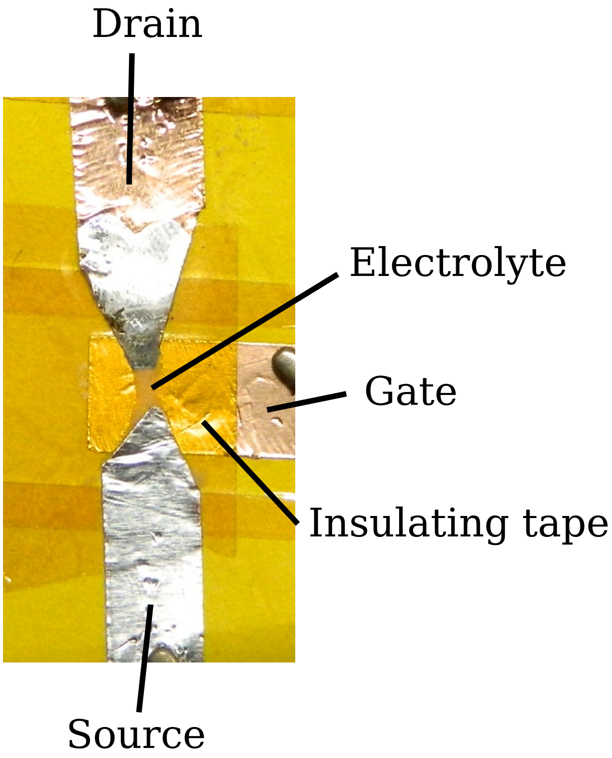

Figure 23: Failed ionic transistor: FET AER hybrid.

According to the theorised chemistry of AEDs (see section 4.2.3) both negative and positive ions (charges) are dissolved into the solution. Both of these types of charge will be able to freely move.

When a channel containing both positive and negative charges is biased the charges do not move away from each other to remote locations. Instead they form a two-layer construction spanning the channel, as shown in figure 24. The carriers continue to span the channel regardless of whether or not a bias is applied, so the device remains conductive.

6.2.4 Experiment: dual-charge channel control ionic FET

A two-gate device was constructed as per figure 25.

The dual-gate design aims to pull both charges of ion toward the centre of the channel, making the far ends less conductive.

Sidenote: a dual-gate device type could potentially be used in a fully differential fashion, allowing the designer (to a limited extent) disregard gate-source or gate-drain voltages.

Results This device did not show any modulation of channel conductivity even when the gates were taken to 30VDC of each other with an isolated power supply.

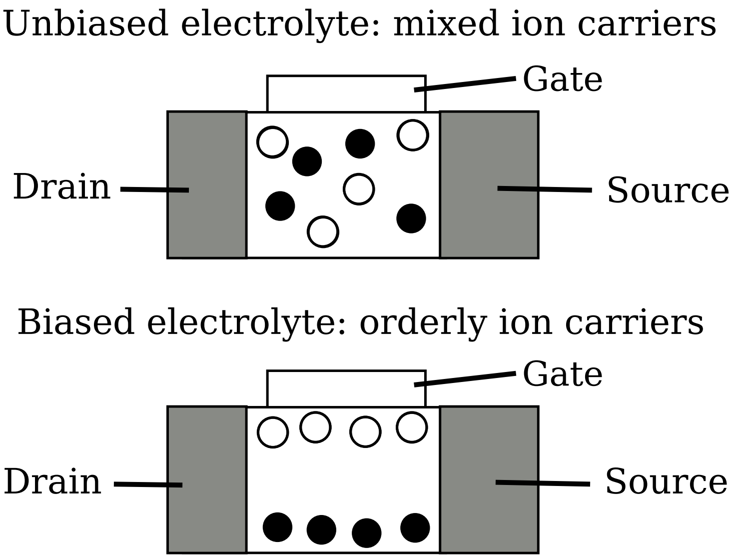

Figure 24: Charge arrangement behaviours inside mixed-charge channels.

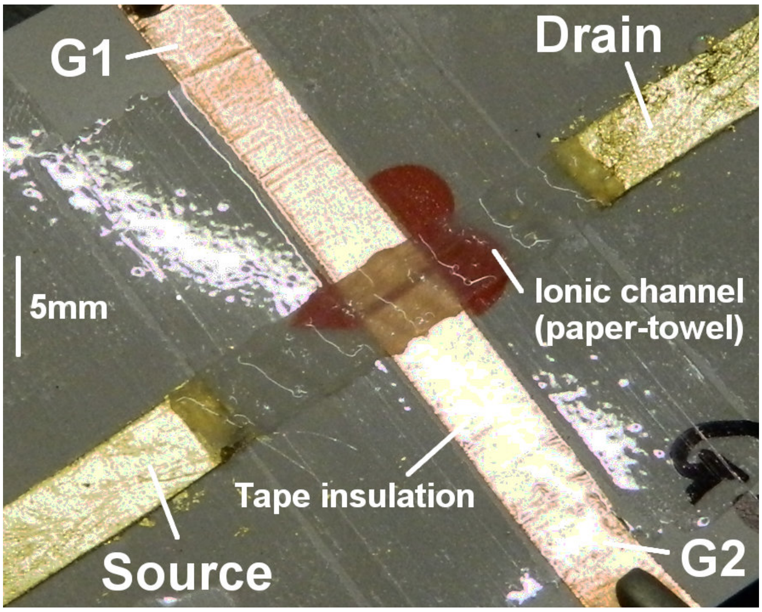

Figure 25: Dual-gate ionic FET. Gates are copper foil, insulated by transparent sticky-tape (40um). Source and drain are gold leaf on adhesive. Channel is $NaHCO_3$ electrolyte in a thin piece of paper towel (to maintain shape).

Discussion It is hypothesised that for this device to work then all of the following must be satisfied:

1. A much shorter channel must be used with a much lower overall amount of dissolved ions.
2. A non-linear channel shape must be used, where ions are dragged into side-lobes of the channel (outside of the primary conductive path). It is theorised that changing the charge distribution of a rectangular path (as used in this experiment) will not otherwise affect overall path resistance unless heavily non-linear effects are discovered.
3. Higher gate drive voltages and thinner tape insulators, preferably by more than a factor of 10x each.

6.2.5 Conclusions

Macros-scale insulated channel modulation devices (macro-FETs) have not been proven to work. If they are possible then they can only be realised with much thinner insulators and much higher drive voltages than those used here.

If these devices do work then they are unlikely to be compatible with the low-technology and high-accessibility goals of this thesis, due to the requirements of high voltages and more exotic insulator materials.

6.3 BJT-style linear layout transistors

This experiment attempted to recreate the simplified models of bipolar-junction transistors, but on a larger scale.

This device failed to perform as a "useful transistor", however its failure required an interesting analysis to prove, motivating the Transistor Proofs section of this thesis.

6.3.1 Experimentation

Aim To determine if BJT-style operation could be obtained by connecting two aluminium electrolytic diodes (similar to BJT P-N junctions) with a shared pool of electrolyte.

Method A two-junction device was assembled as shown in figure 26 using:

1. A slide transparency for the substrate
2. Aluminium foil for the base electrode, adhered using thin double-sided tape.
3. Gold leaf for the collector and emitter, adhered using thin double-sided tape.
4. Ordinary clear sticky-tape and yellow-tinted Kapton tape[16] to contain liquid boundaries[17].

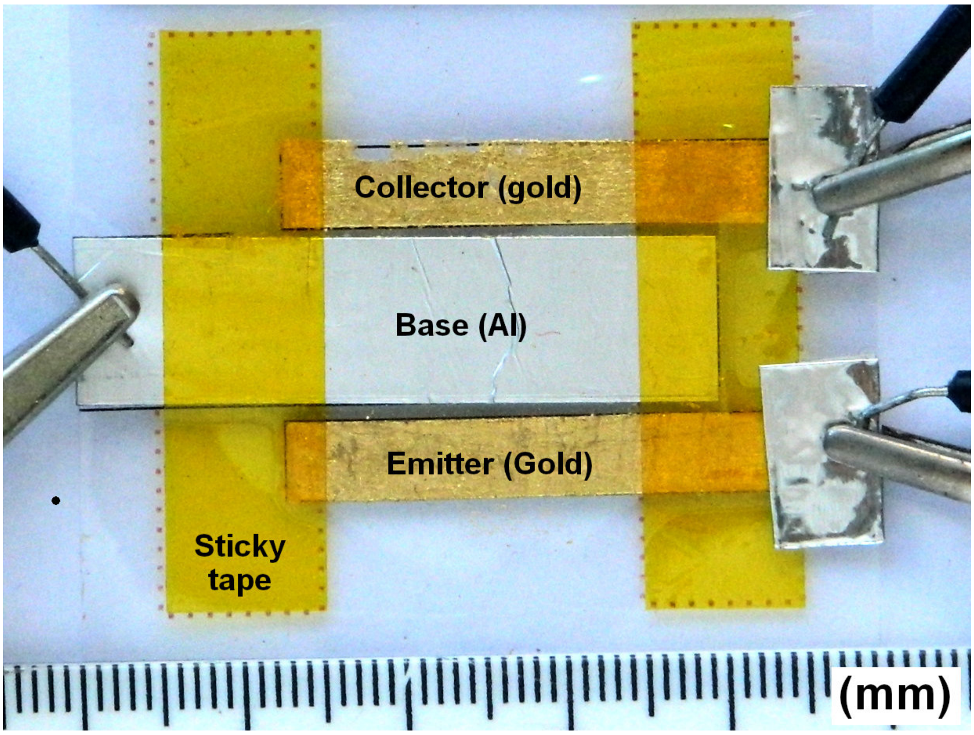

Figure 26: BJT-style device (shown before the electrolyte solution was applied to bridge the three metal contacts). 10x20mm aluminium sample shown, thinner dimension devices were also tested.

A 0.01 molar solution of NaHCO3 was chosen arbitrarily for testing. Concentration experiments are documented in section 4.4.

The device was placed in a test circuit as described in section 6.1. A 12V overall device and load voltage was chosen to be arbitrarily above the known 5V turn-on voltage of a single-junction aluminium electrolytic device (Hales 2018). R_B and R_L were both chosen

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[16] The high-temperature endurance properties of Kapton and Kapton-clone tapes are not of useful consequence to any of the tests in this thesis, however they provide a stronger visual contrast than clear tape, making identification of taped areas easier.

[17] Cleaned surfaces of sticky-tape were found to be slightly hydrophobic, allowing electrolyte pools to more easily be contained.

to be $10K\Omega$ initially for the test results shown here, however later R_L was reduced to the smaller value of $1K\Omega$ and the experiment repeated, obtaining similar results.

Voltage measurements were taken by low-cost 830-series clone multimeters, as shown in section 3.2.

Experimental process used:

1. Perturb the gate drive DC supply slightly
2. Wait for the currents and voltages in the system to settle to stable values.[18]
3. Record all voltages.
4. Repeat.

Results Observed measurements jittered noticeably by a few percent. It is assumed this is because of bubbles forming, moving and decaying in the electrolyte.

This device appeared to display power gain (figure 28), which at first was misconstrued to demonstrate useful amplification (see section 5.2 "amplification is not enough"). Further investigation of power, current and voltage curves (figure 27) concluded that this device failed to meet test (1) of section 5.6 and hence is not a useful amplifier.

Errors Two particular anomalous areas of the power curves stand out:

1. Power gain approaches infinity as the base voltage approaches zero. This is an artifact of current bypassing the modulation action of the device and instead always traveling through to the load resistor. Nullifying this quiescent power would be one method of avoiding this numerical problem.
2. A small region of the power versus base current curve appeared to show power in the load changing at a higher rate than power in the base (this region of interested is isolated in figure 29). This is believed to be due to a combination of forcing positive power in the equations used to calculate values for the plots and due to the capacitive action of the device creating temporary "negative power draw" under certain (transient) conditions.

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[18] The (lossy) capacitances of the electrolytic device combined with the in-circuit resistances created RC filters, noticeably slowing the response of the circuit down.

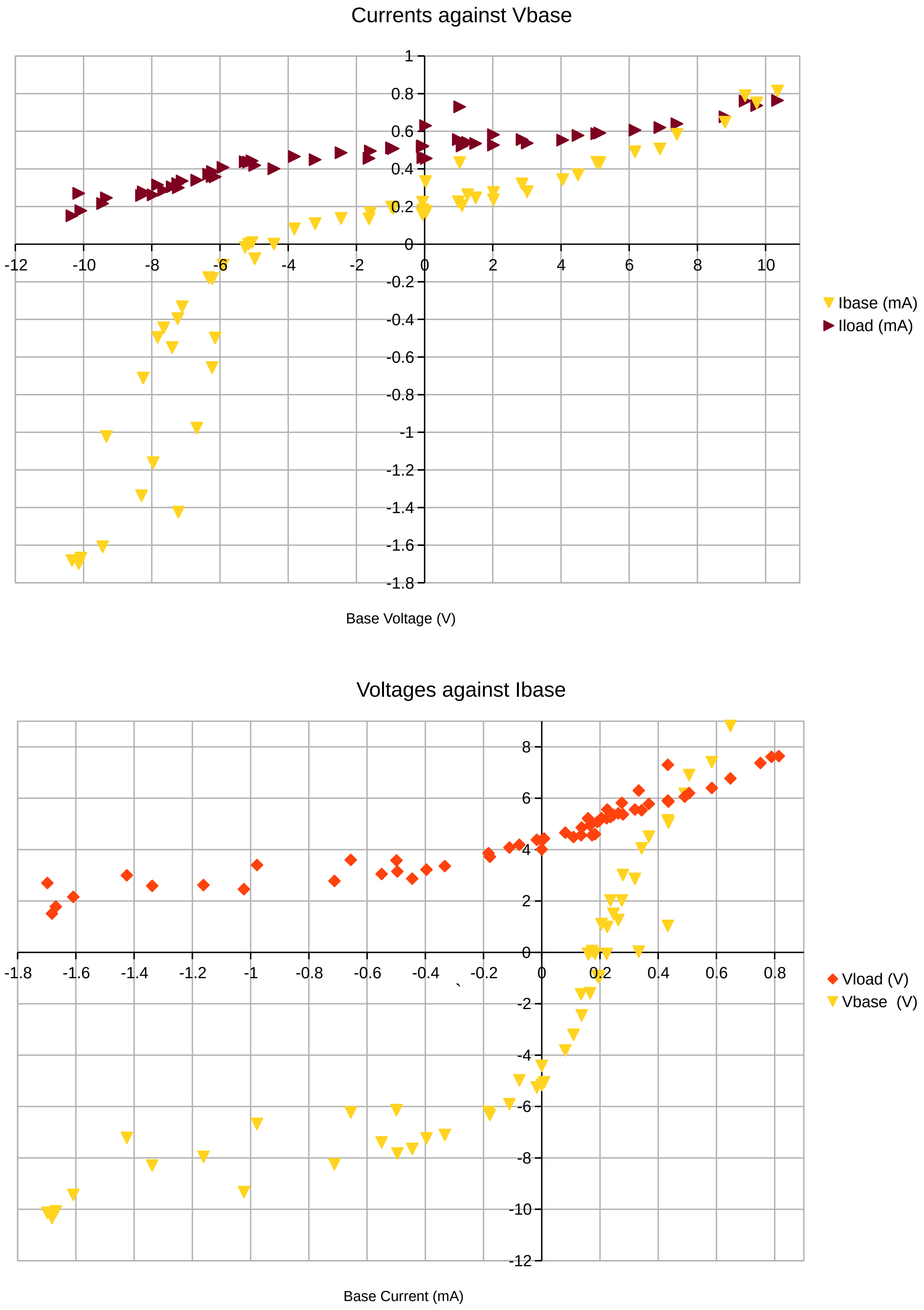
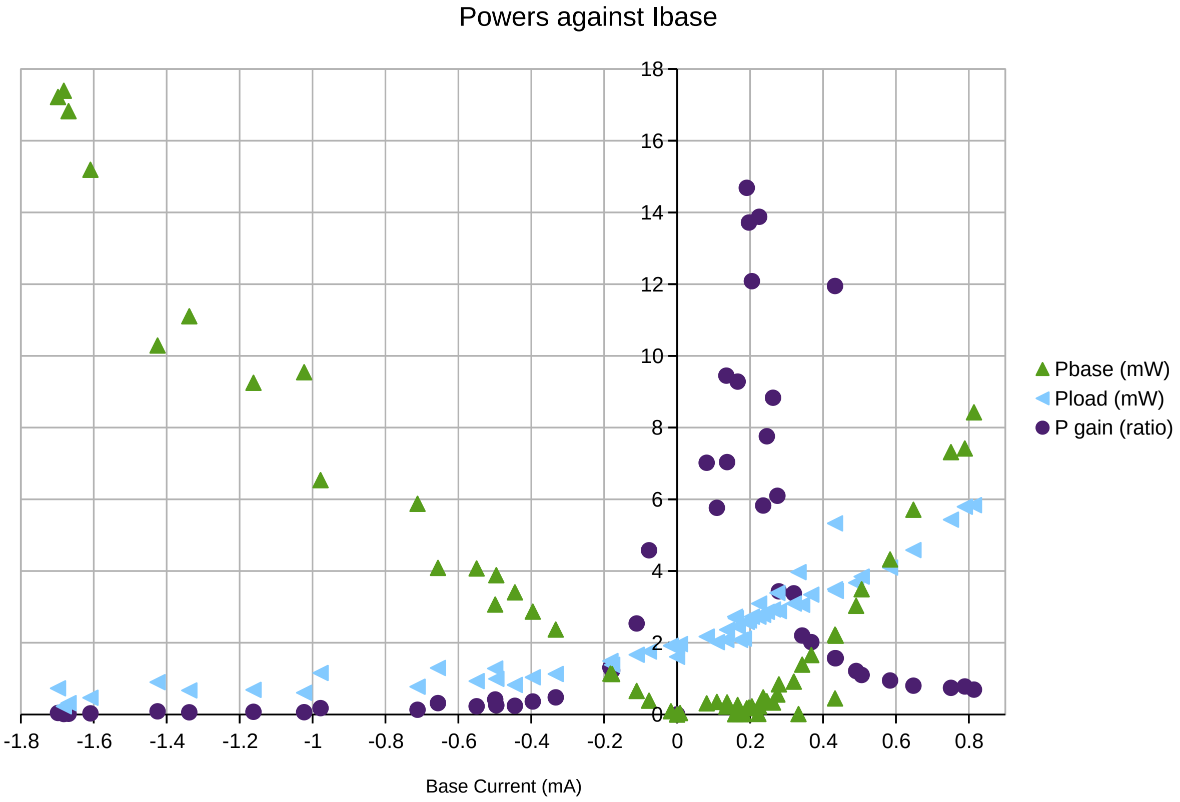


Figure 27: Voltage and current transfer characteristics



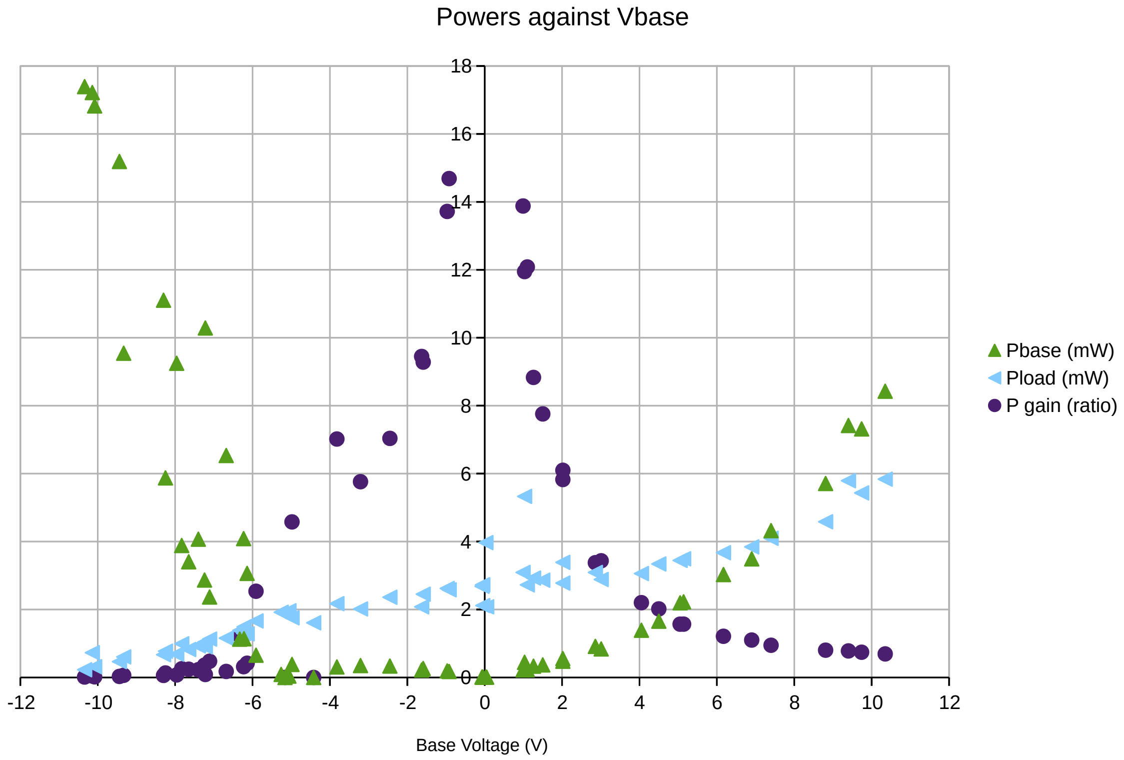


Figure 28: Power gain characteristics, plotted against the two (similarly shaped) input parameters. These graphs are horizontally distorted variants of the same data, both are included so that more regions of interest (eg base voltage=0) can be observed.

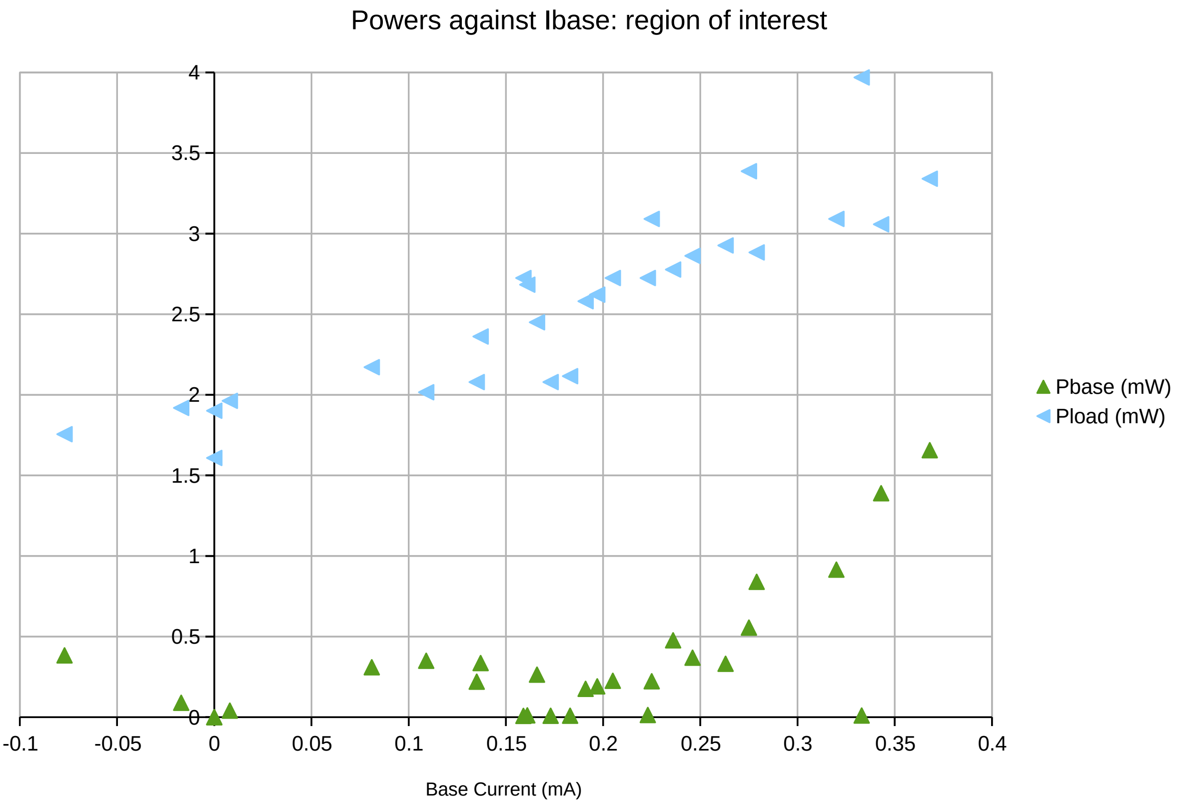


Figure 29: One particular region of interest from the power vs Ibase plot in figure 28. The load curve is shown to have a higher gradient than the input curve around 0.05 to 0.20 mA of base current.

6.3.2 Conclusions

This device appears to be a non-linear voltage divider (attenuator), not a useful transistor.

If any transistor-like characteristics of this device existed then they were obscured by the strong effects of the diode junctions in the device, likely due to the device's large geometry. This device could potentially be modelled by a weak (high-impedance) transistor superimposed upon a multi or single diode structure.

Alternatively it could be considered that this device only has a single diode junction: a single layer of aluminium oxide + hydroxide on the single aluminium contact, and that its performance could be similar to a diode feeding the center of a resistive voltage divider. Attempts to SPICE simulate such devices have unfortunately resulted in dramatically different response curves, a model of a diode with a very gradual turn-on is likely required.

6.4 Interdigitated concentration control transistors

After the failure of the linear BJT-style device a new "inverted" geometry was designed with the intention of creating a device that modulates the channel impedance based on electrolyte concentration. See figure 30 for an example device. The aluminium electrode was intended to interact with the electrolyte, pulling ions out of solution into solid form (the aluminium oxide-hydroxide layer) and visa-versa. Changing the concentration of the electrolyte was expected to change the impedance of the channel.

This geometry is considered inverted compared to the last experiment because it changes:

- The large distance between the two channel electrodes into a very small one.
- The small distance between channel electrodes and base into a very large one.

The design aim was to prioritise the electrical interactions between channel contacts (channel modulation effects) and minimise the direct electrical interactions with the base electrode (dual-diode effects). The base electrode should only be used as an "electrically remote" method of changing device concentration.

This device design is a form of redox-device, as researched in section 2.2.4.

6.4.1 Initial experimentation

This device showed similar results to the BJT-style linear device in the previous section, with the diode effects dominating and no usful amplification being detected in a +/-30VDC aluminium electrode swing range.

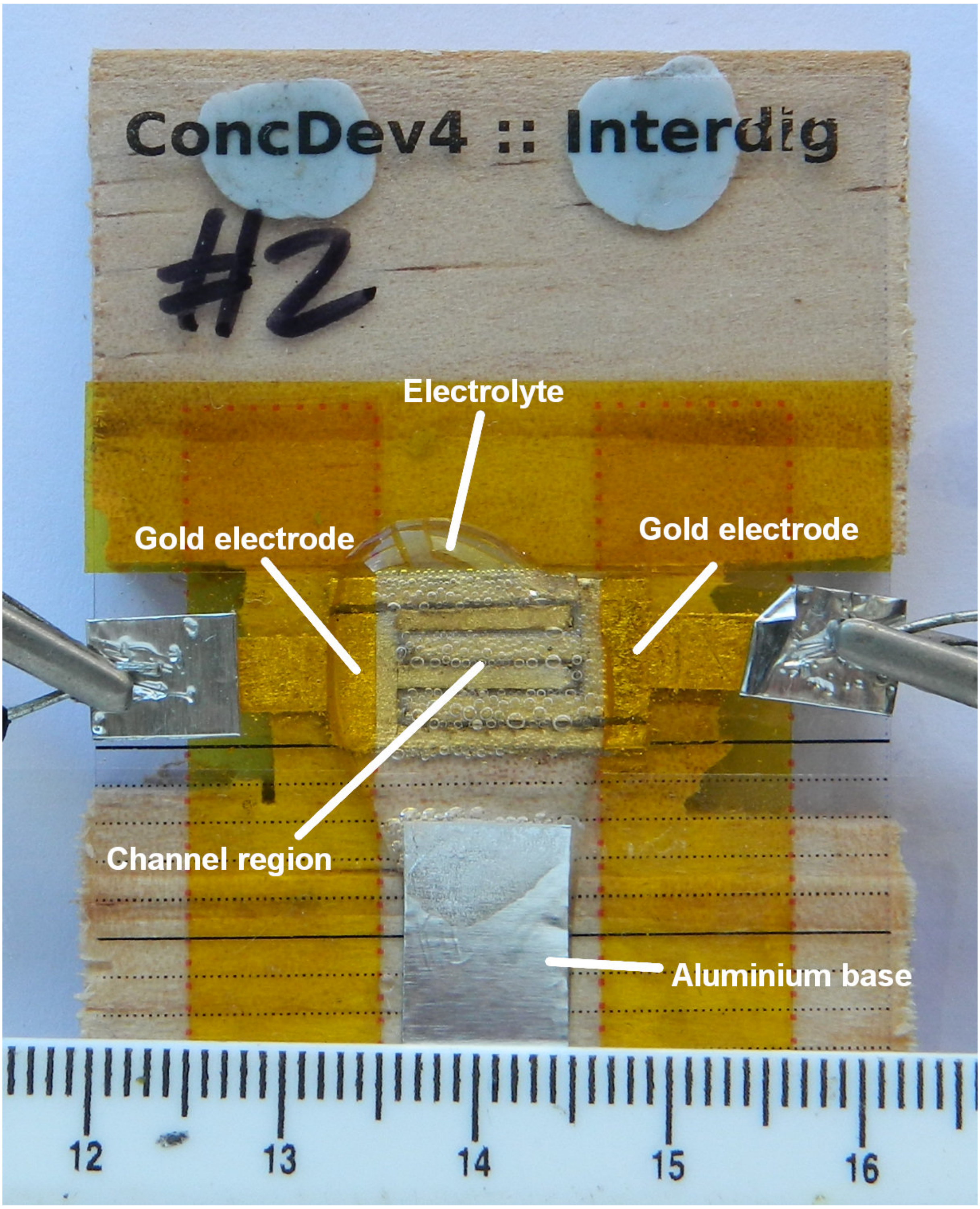


Figure 30: Interdigitated concentration control device. Shown during a test with electrolyte applied (note the bubbles on one gold electrode). This photograph shows uncontrolled aluminium surface-area contact, a problem resolved with more insulating tape in further experiments.

The primary hypothesis for this result was that the total amount of ions dissolved into the solution was too large compared to the amount that could be sequestered into a solid oxide/hydroxide film form. In other words: only a tiny percentage of electrolyte concentration was being modulated.

An alternative hypothesis was that the electrical effects between the base and the electrodes was still more powerful than the electrical interactions between the electrodes themselves.

6.4.2 Higher surface-area aluminium

A high-SA aluminium electrode was fabricated by roughly sintering fine aluminium powder onto aluminium foil. A small butane pencil torch was used as the heat source.

Unfortunately this process was only marginally successful, with the majority of powdered aluminium not successfully adhering. Sintering of metals that easily oxidise is not easily achieved.

During testing this electrode revealed similar results to prior tests. Additionally it appeared that this electrode was heavily oxidised, likely sealing much of the new surface away from electrically interacting with the electrolyte anyway.

Future work should consider better and easier ways of increasing aluminium surface area, such as acidic etching. Such methods have a large amount of published literature and are within the reach of this thesis' target audience.

6.4.3 Isolated four-terminal drive: removing direct electrical influences of the base

Another failure hypothesis was that the AER chemistry is fundamentally incompatible with concentration-control devices.

Sodium bicarbonate forms a buffer solution when dissolved in water. This buffer counteracts changes to solution pH (see section 4.2.3 for chemical equation detail).

If the aluminium is removing species from the solution that affect its ph (eg OH- ions) these species may be getting replaced from other sources, such as from the electrolysis of the water itself on the device's electrodes (visible as minor bubbling).

To test this theory a four-terminal variant of the concentration control device was developed where the section of the device changing its concentration was galvanically isolated from the electrodes either side of the channel. Schematic of this test provided in figure 31.

This device failed to show any useful channel modulation, meaning that either:

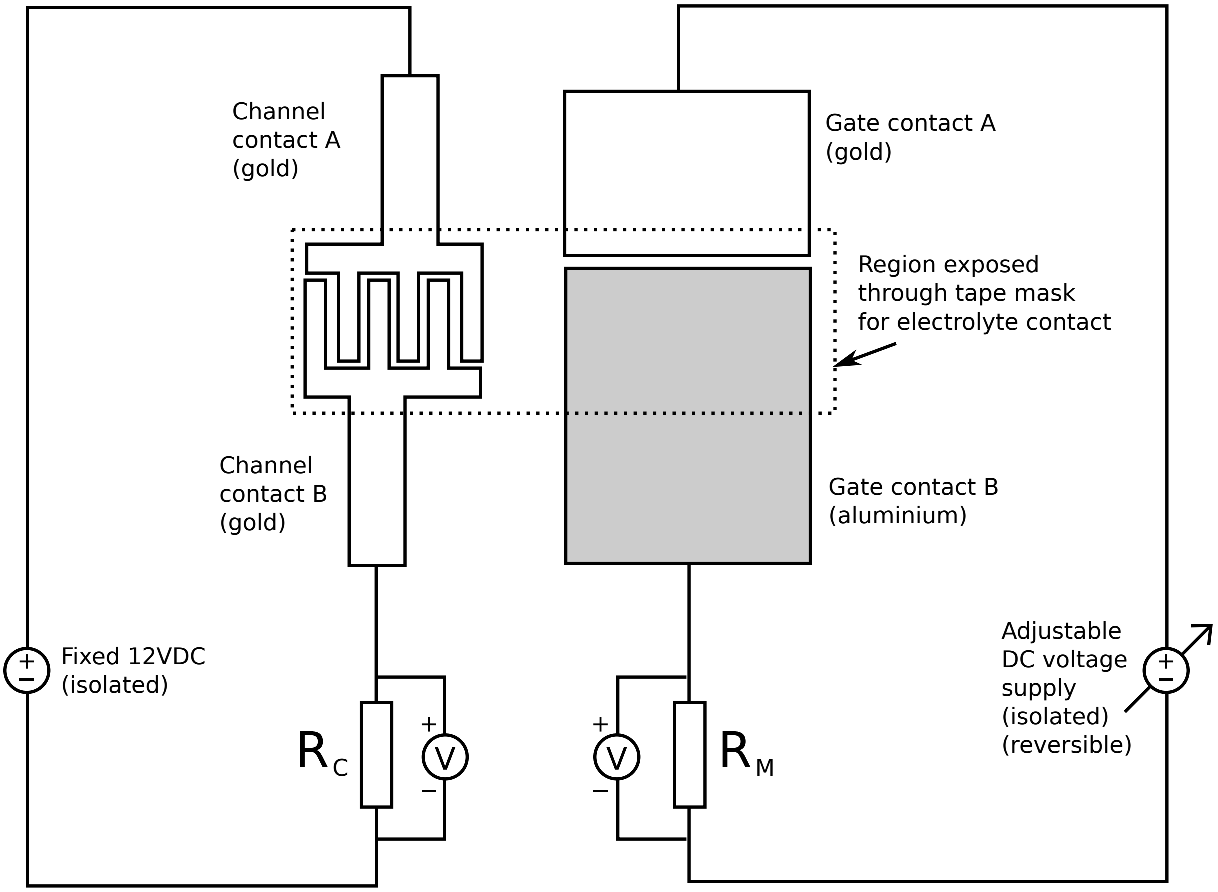


Figure 31: Four-terminal concentration control device

1. This chemistry fundamentally makes it difficult for the concentration of the electrolye to be modified electrically (eg through a chemical-buffer action).
2. The amount of ions being taken in and out of solution is still too small to affect the solution's conductivity.

6.4.4 Conclusions

Concentration control transistors have not been proven outside of papers such as Letaw and Bardeen 1954 (now considered a questionable source, see section 5.7.1).

A priority on future experimentation should be recreating these devices with:

1. Lower concentration solutions (see section 4.4)
2. Different chemistries (other electrolytes listed in 4.1.2 or Letaw and Bardeen's ferric-ferrous couple)
3. Higher surface-area reactive (ie aluminium) electrodes (through processes such as acid etching).

One particular method of meeting points 2 and 3 would be to use steel wool as the reactive electrode with Letaw and Bardeen's ferric-ferrous couple. Initial testing has proven this is difficult, with the steel wool wicking up electrolyte during experimentation and (counter-productively) requiring larger volumes of electrolyte to be used.

7 Aluminium Electrolytic Light Emitting Ionic Devices (LEiDs)

Whilst researching AER diodes it was discovered that these devices can glow under certain conditions. This section investigates how this can be adapted to intentionally exploit this glow as an output indicator, similar to how LEDs are used in modern circuits.

These devices are demonstrated to work, however their performance and operational requirements make them incompatible with other researched technologies of this thesis.

7.1 (Part A) Introduction and prior work

The cathode of an AER can faintly glow a green-blue colour under certain conditions (Kruse 1922, Heffner 2006, Steiner 2003). The only known photograph of this effect (prior to this thesis) is in figure 32.

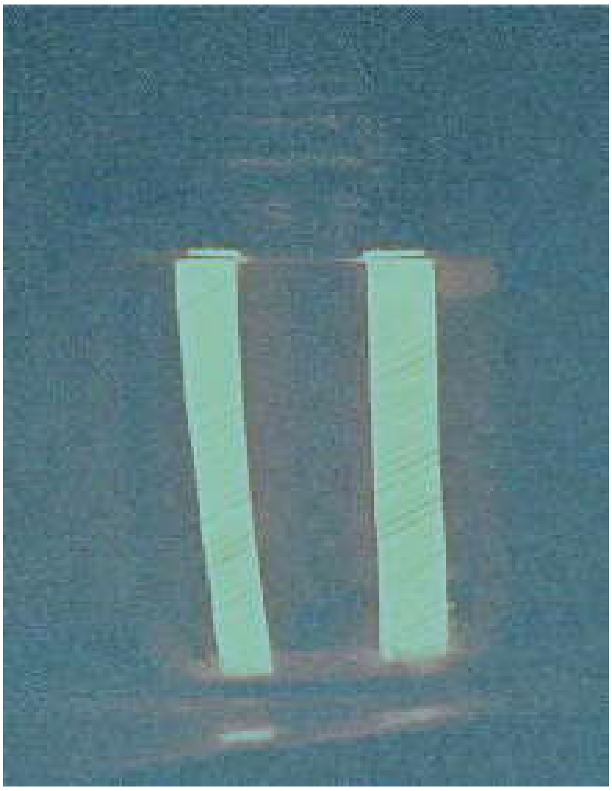


Figure 32: Glowing aluminium cathodes in an AER (Steiner 2003).

The exact process that creates this glow is unknown. Heffner hypothesises that the large electric field across the insulating aluminium oxide layer is causing electrons or ions to tunnel and recombine; creating light in a manner similar to light emitting diodes. Given the mono-chromatic appearance this may be correct.

An attempt was made in part A to recreate this glow effect, however only the “failure” or “overloaded” mode of operation (see section 4.1.4) was observed. Instead of glowing evenly the aluminium cathodes appeared to sparkle at the edges, and eventually the aluminium foil was “cut” by this destructive process. See figure 33 for a photograph.

Figure 33: Overloaded-mode operation of an AER.

It was hypothesized that this failure was caused by the use of impure materials (household aluminium foil, household cooking sodium bicarbonate) and inappropriate forming methods (too quick of a voltage rise). In the part B experiments detailed below better materials and equipment was used to combat this problem.

7.2 Glow under AC drive

7.2.1 Aim

To determine if:

- Glowing devices could be achieved as per the literature
- Purity and surface areas of ingredients affected performance

7.2.2 Method

Anti-series diodes were constructed by omitting the inert metal electrode in the AER devices and instead using two aluminium electrodes, as shown in figure 34. This layout suggested by Steiner (2003) permits full AC drive to be applied to the device without having to worry about reverse currents "shorting" the device out and expending large amounts of energy.

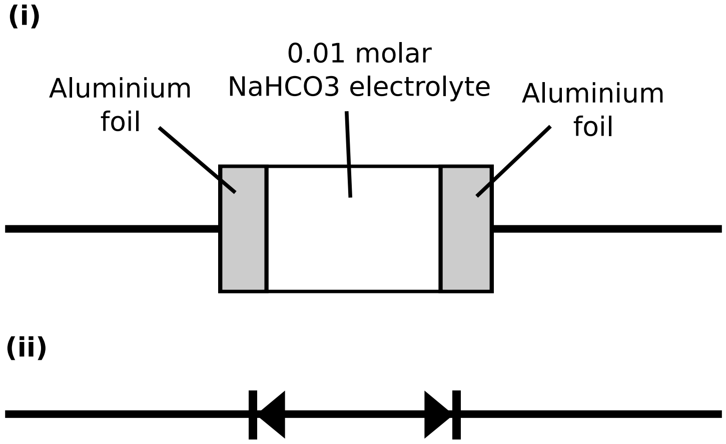


Figure 34: Anti-series AER. (i) shows the physical construction and (ii) shows the equivalent electrical model. The aluminium-electrolyte interfaces are where the oxide/hydroxide layers form, so these interfaces provide the diode functionality.

Rather than using a ballast lightbulb in series with a fixed AC supply (as per research in part A) a variac was employed[19] to adjust the AC voltage applied to the device. A full experimental circuit diagram is in figure 35.

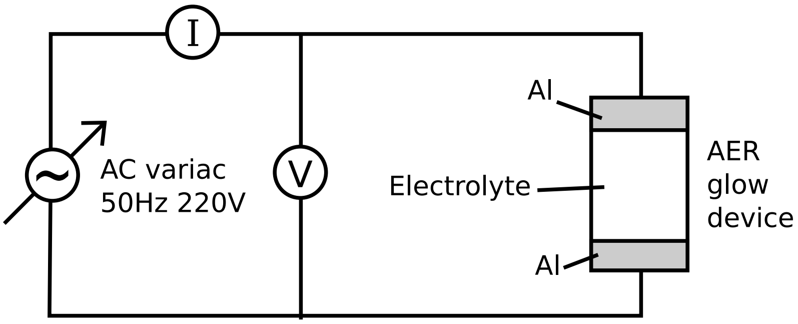


Figure 35: Variac-driven AC test circuit for AER glow.

Devices were constructed on plastic substrates as per the method described in section 3.3.

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[19] Safety note: most variacs are capable up providing voltages up to line line (230VAC at 50Hz) and as such present an electrocution hazard. Proper isolation (ie through an isolation transformer), safe experimental procedures and tertiary protection (ie RCDs) are worth considering before attempting to re-create this research.

A photograph is provided in figure 36. Three difference types and sources of aluminium were used:

- Multix-brand kitchen foil, shiny side.
- Multix-brand kitchen foil, dull side.[20]
- Unbranded generic pre-made aluminium tape (“Roll Al”), linearly textured.

During testing the voltage of the variac was started at zero and slowly increased to ensure:

1. The oxide-hydroxide layer on the devices was formed correctly. Sudden increases in current would “foul” this process and create that devices that shorted out.
2. Overall power dissipation in the device was limited, to avoid boiling and deformation of the plastic substrate.

AC current readings through the device were monitored to ensure the average current did not exceed a few mA. Each experiment required a few minutes of slow and steady variac adjustment to stay within this guideline.

7.2.3 Results

Devices would slowly increase their impedence over time as they formed. No optical effects were noted until voltages reached the 90-110VAC RMS range.

Once at this range devices would start to glow a faint white colour, as depicted in figure 37 and figure 38.

Devices would very slowly dim over the course of a few minutes, however increasing the voltage counter-acted these effects. If voltage was increased too quickly then power also increased until devices boiled, requiring a reduction and voltage.

Devices operated up to mains line voltage (230VAC RMS) without issue. No evidence of arcing or other failure modes at these high voltages occurred provided the devices were slowly formed up to this point over several minutes.

Both the dull-side of the kitchen foil and the pre-made aluminium tape performed similarly. The shiny-side of kitchen foil was noticeably dimmer in all tests.

A maximum lifetime of the devices was not observed, the electrolyte would dry out before the samples would otherwise stop glowing.

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[20] Most kitchen foils have a “dull” side and a “shiny” side. It is believed this is caused by rolling two sheets of the foil together during the final stage of manufacture, where the sides touching the steel rollers become the shiner of the two.

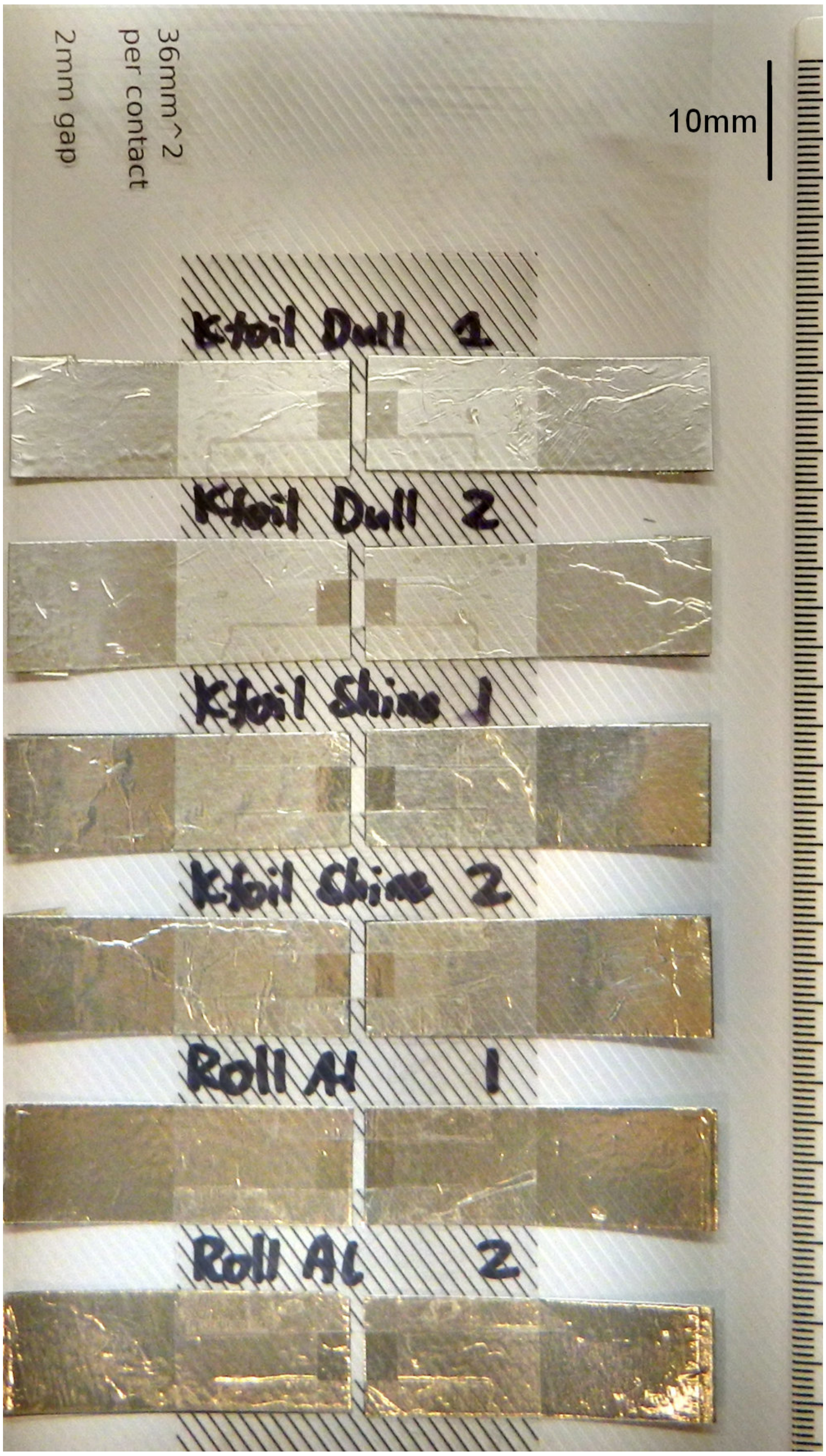


Figure 36: Stenciled array of aluminium-aluminium devices. Note the use of clear sticky tape to mask off everything but two central rectangles (per device) for electrolyte contact.

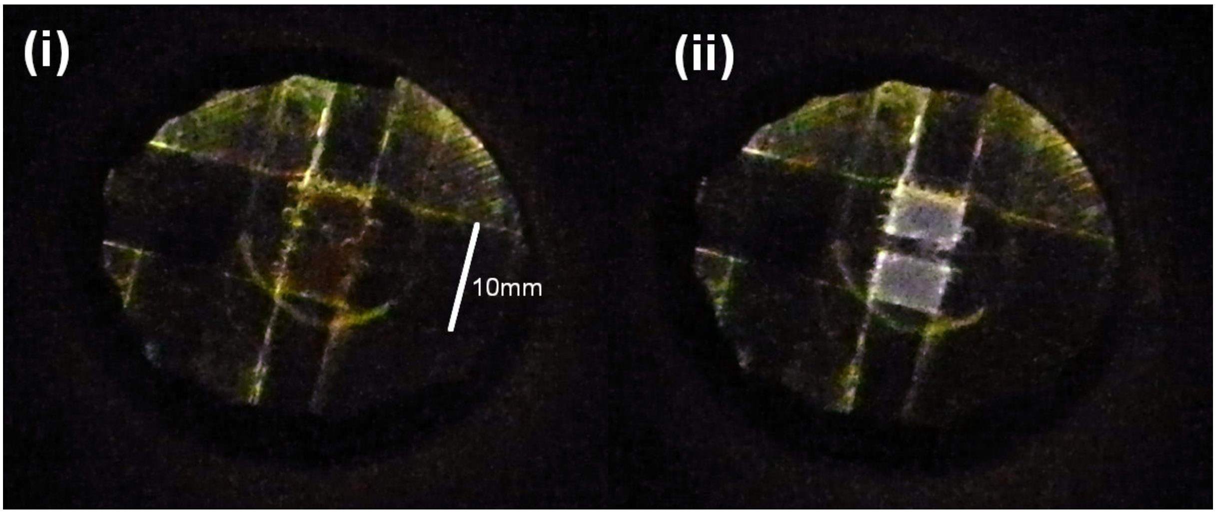


Figure 37: One of the stenciled devices shown in figure 36, (i) without any voltage applied and (ii) with 100VAC applied. Item was photographed through a cardboard tube, some (greenish) external light notably still leaked in between the tube and the stencil. High image noise and poor colour reproduction are due to the short camera shutter time & instability of the cardboard tube apparatus.

7.2.4 Discussion

These results varied greatly from the literature reviewed in section 7.1:

- The light emitted was white, not green
- Around 100VAC and higher were required, compared to the lower numbers (~40VAC) quoted for this chemistry (in section 4.1.3).

A white light cannot directly be created by a traditional bandgap-style LED device. Instead the operation of these devices is theorised to be either from:

- Multiple band-gaps (due to the complex aluminium oxide and hydroxide layers) combining to create white.
- Exothermic oxidation of the aluminium (a more controlled version of “sparks”).

The higher activation voltage is believed to be caused by the use of purer ingredients. The green glow observed in prior works may be due to impurities found in the water, aluminium or sodium bicarbonate used.

The difficulty of “shiny” aluminium foil to provide the glow is believed to be related to surface area (SA). Shiny samples are flatter with less SA, dull or textured samples have a higher SA. If it is assumed that the amount of glow is associated with the amount of SA then these results make sense.

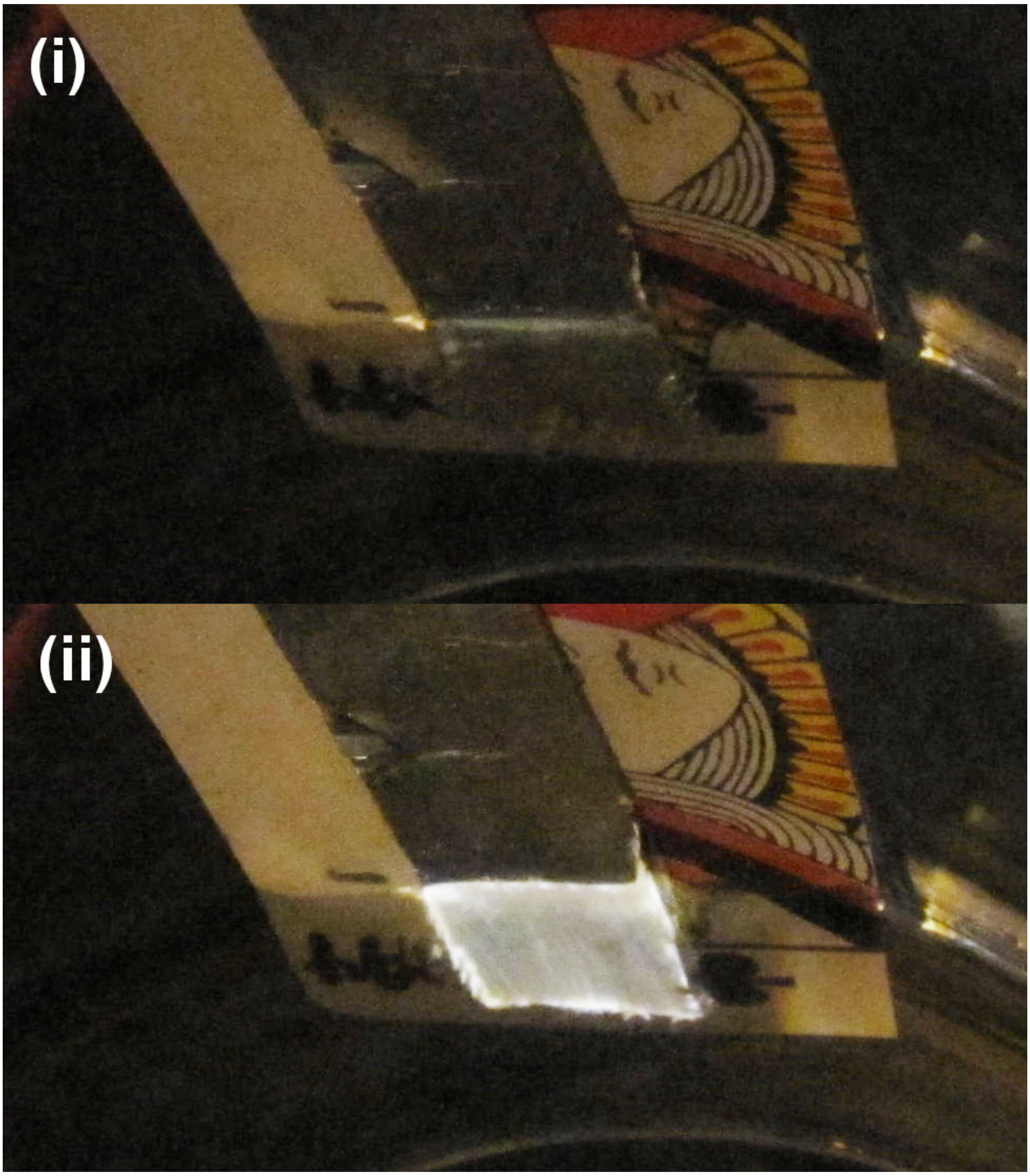


Figure 38: Glowing aluminium electrode in a beaker-based test, (i) without any voltage applied and (ii) with 100VAC applied. The second aluminium electrode is not pictured. Photographed at night using a 1-second (long) exposure from a properly mounted camera. Actual glow is dimmer than this photo suggests, however it is much brighter (from all viewing angles) than would be possible just through reflection of the (minimal) unwanted external lighting.

Overall these devices, in their current forms, are not compatible with the goals of this thesis:

1. They require high voltage to operate, which are both unsafe for beginner educational use and inconvenient to work with.
2. They are dim enough to notably reduce accessibility, requiring night-time operation or shrouds to view.

7.3 Glow under DC drive

DC is more practical to obtain and use in many IC contexts, as well as generally safer for beginner experimentalists to handle. As such it was important to determine whether or not these devices could operate under DC conditions.

Samples used in the previous experiment (AC drive, section 7.2) were re-used. High DC voltages were obtained through a "joule-thief" style circuit followed by a voltage multiplier and rectifier, as shown in appendix item 12.3.

7.3.1 Results

Experiments were performed quickly as the power supply overheated if run for more than a few seconds. Exact voltages were in the 100-200VDC range, with notable AC spikes superimposed, but exact readings were not practical to make.

Under certain conditions it was possible to make one (of the two) aluminium contacts in the samples glow, however this would only last several seconds before fading away to nothing, presumably becoming damaged.

Returning these devices to AC operation revealed that the damaged aluminium contact continued to stay unlit, whilst the unused aluminium contact lit as per normal.

7.3.2 Discussion

It appears that under AC conditions the oxide-hydroxide film junction layer is self-repairing, whilst under DC conditions it is destroyed. Fundamentally it appears that DC operation of these devices is not practical.

7.4 Additives

Other chemicals were added to LEiDs whilst they were operating under AC bias to try and determine if the colour or threshold voltage of the LEiDs could be adjusted to what is mentioned in literature.

The following changes were attempted:

- More sodium bicarbonate (increasing the conc above 0.01molar)
- Sulphuric acid (H_2SO_4)
- Copper (solid electrode -> dissolving in)
- Table salt (NaCl)

In almost all cases the devices proceeded to short out, leading to sparking, melting, boiling and failure.

Increasing the sodium bicarbonate concentration is known to work from previous experiments (well beyond the 0.01 molar level), however if any solid (un-dissolved) material lands on active aluminium electrodes then the devices begins to break down and start sparking. The sodium bicarbonate appears to chemically react with the aluminium and create other, unwanted products, as shown in figure 39.

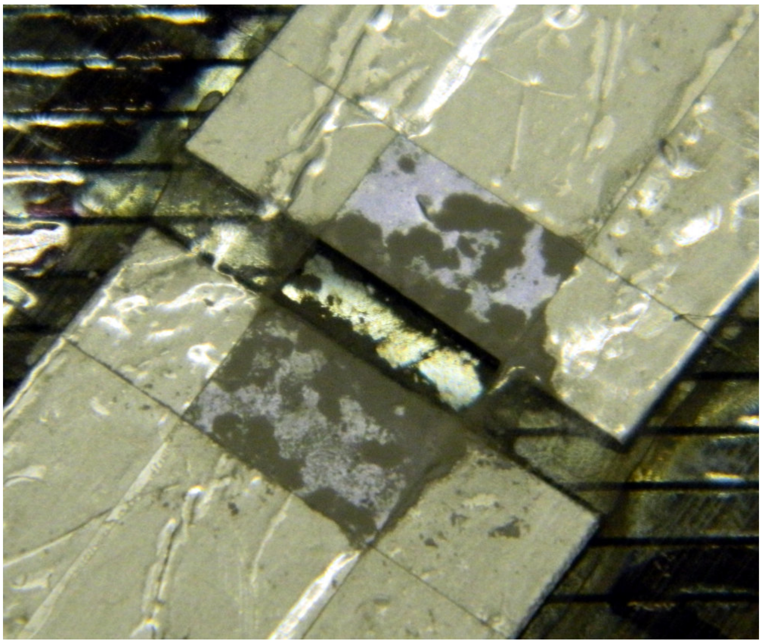


Figure 39: Chemically bonded deposits of excess sodium bicarbonate on an aluminium-aluminium sample after testing. Device dried and cleaned before photographing.

Better additives ("dopants") need to be chosen and researched. Additionally it may be necessary for these additives to be in the solution used for initial forming, rather than being added after, so that the oxide-hydroxide layer growth is affected by their presence and they are fully dissolved before undertaking any electrically-driven reactions.

7.5 Theoretical Compatibility with Al-Bicarb transistors: circuitry and drive considerations

The high voltages required to light aluminium LEiDs makes them difficult to electrically interface with theoretical Al-Bicarb transistors.

Consider the circuit in figure 40:

- When the transistor is turned on (low-impedence) it only has to deal with a small voltage drop.
- When the transistor is turned off (high-impedence) it has to block a much larger amount of the supply voltage. At a certain voltage it will start glowing or failing itself instead.

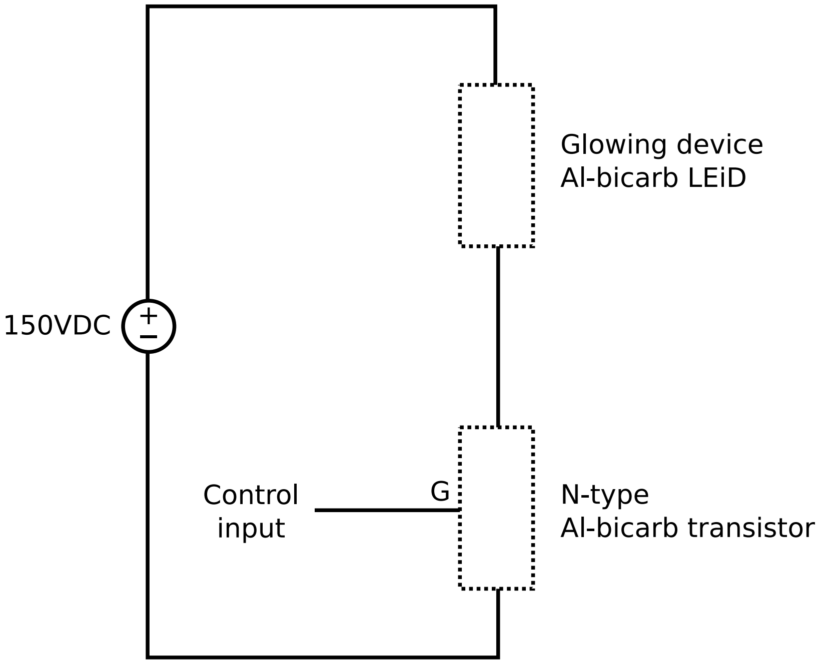


Figure 40: Theoretical circuit for switching LEiDs on and off using similar-chemistry theoretical transistors.

The maximum voltage load for each switching device could potentially be resolved through the use of multiple series transistors and multiple gate-drive power supplies, however this would be very inconvenient to layout and potentially impossible to switch/control from a single aluminium-bicarb technology circuit.

If the al-bicarb transistor can successfully be used to “transfer” the glow effect from the two-terminal LEiD to the three-terminal transistor then the device will still be useful. The transistor could be covered, ignored or exploited as a “flipped bit” light. This however depends on the transistor being able to reliably drop more voltage than the LEiD when in the off state, which may be possible through the manipulation of relative dimensions (ie making the transistor smaller and higher impedance than the LEiD).

7.6 Conclusions

In their current form LEiDs are not compatible with the goals of this thesis. Notably they are:

1. Unsafe: requiring high AC voltages
2. Inconvenient: glowing only dimly
3. Incompatible: unlikely to be drivable using ionic transistors theorised so far.

Further research should focus on:

1. Trying different electrolyte solutions (from the many options listed in 4.1.2).
2. Trying additives suspected to be unintentionally included in original 1920’s experiments (to reduce operational voltage)
3. More understanding of the film growth process and how it could potentially be “healed” or “re-used” at DC.

8 Further Transistor Concepts

8.1 Bubble-control Transistor

Bubble-control is a theoretical method of modulating the conductivity of fluid channels through the use of bubbles that are (normally) parasitically created by the electrolysis of water. See the photographic of an example in figure 41). This concept of transistor control is theorised based off observations made during the research of other transistor designs during this thesis, however this method has not yet been tested.

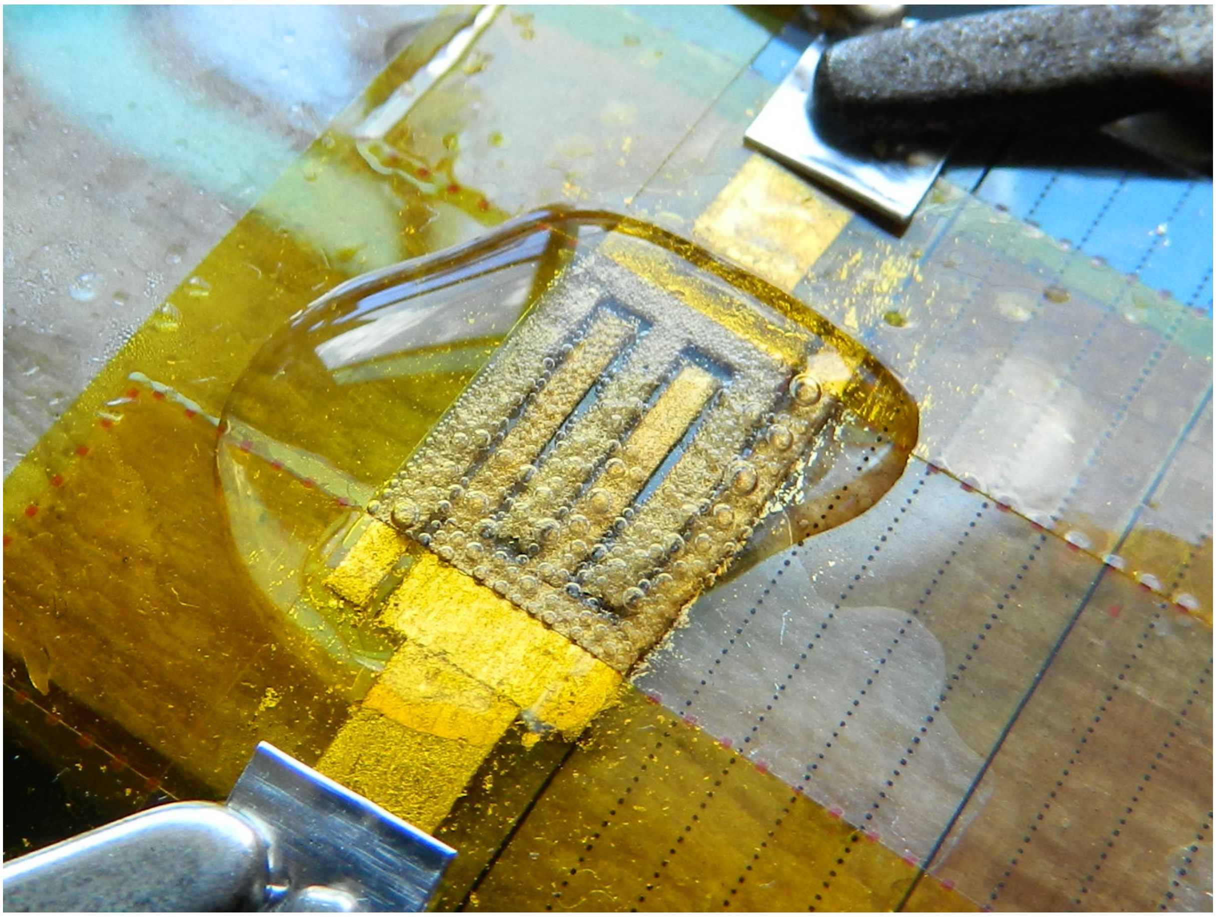


Figure 41: Bubbles developing on electrolyte contacts during DC operation.

It was observed that these bubbles increase the impedance of ionic devices. Gently removing these bubbles (through the use of a small tool such as a tooth-pick) instantly reduces device impedance.

It was also observed that these bubbles could be moved and controlled through the application of voltages to electrodes. Bubbles would transit from one electrode to the other even when the other electrodes were from isolated power supplies, suggesting static charges (from localised ion or gas concentrations) may be the mechanism driving this movement.

It is hypothesised that devices could be made that intentionally create and control these bubbles to manipulate the impedance of the ionic channels, potentially making transistor-like devices.

Potential research topics: microfluidic transistors and microfluidic bubble transportation.

8.2 Resonant Tunnel Diode Logic

Resonant tunneling diodes can be exploited to create memory cells and logic circuitry (Ling 2006).

Whilst AER devices sometimes appear to show a V-I curve falloff similar to a tunneling diode (such as hinted in figure 44), these behaviours when operated at higher voltages are self-healing. ie the devices “form” to a better level and the behaviour disappears.

If other diodic devices could be developed that exhibit stable tunneling behaviours then amplification and logic using these devices could be considered as an alternative pathway to achieving the goals of this thesis.

9 Project Conclusions

Whilst this task has failed to achieve its hardest goal (a working low-technology “useful” transistor), it has still achieved most of an IC technology (working diodes, substrates, capacitors and resistors) using only low-technology methods.

Several new topics of interest have also been brought up during this thesis, including:

- Simple ingredient ionic light-emitting devices (LEiDs).
- The prevalence of poor transistor proofs in published scientific works.
- Digital logic circuits using simple aluminium-bicarbonate ionic diodes.
- Pressure and humidity sensitive resistors using household ingredients.

Transistor fabrication is a difficult task even with the strict process controls used in industry. This thesis’ strategy to overcome this problem has been to combine vastly disparate sources of information and device designs in order to make new hybrid devices at a macro scale. The areas left to research are extensive, however the experiments in this thesis have identified some key pathways that should be used for future research.

Part II

Appendix

10 Interesting findings unrelated to aims

10.1 Varying AER film thicknesses & colours

Discolouration of aluminium contacts was noted after samples were used (formed), cleaned and dried; as shown in section 12.3. Films ranged from blue and green to pink and yellow.

It is hypothesised that these colours are caused by thin-film interference. The aluminium oxide and hydroxide layers above the aluminium for each sample are all of different thicknesses and structure do to the different speeds of forming and tests performed during their lifetimes.

It is theorised that these colours may be useful for determining the thickness or "health" of junction forming, however further investigation into the geometry and makeup would be required to make this a useful strategy.

10.2 Unintentional colloidal gold

After subjecting an interdigitated device from section 6.4 to DC bias on the channel for testing a sample was set aside and partially dried. One set of gold fingers appeared slightly redder than the other, as photographed in figure 43.

After complete drying the colour difference disappeared.

It is theorised that small particles of gold had migrated through the fluid to one of the electrodes and formed colloidal gold (a usually red mixture). It is possible that bubble transport (see section §8.1) caused the migration of these particles.

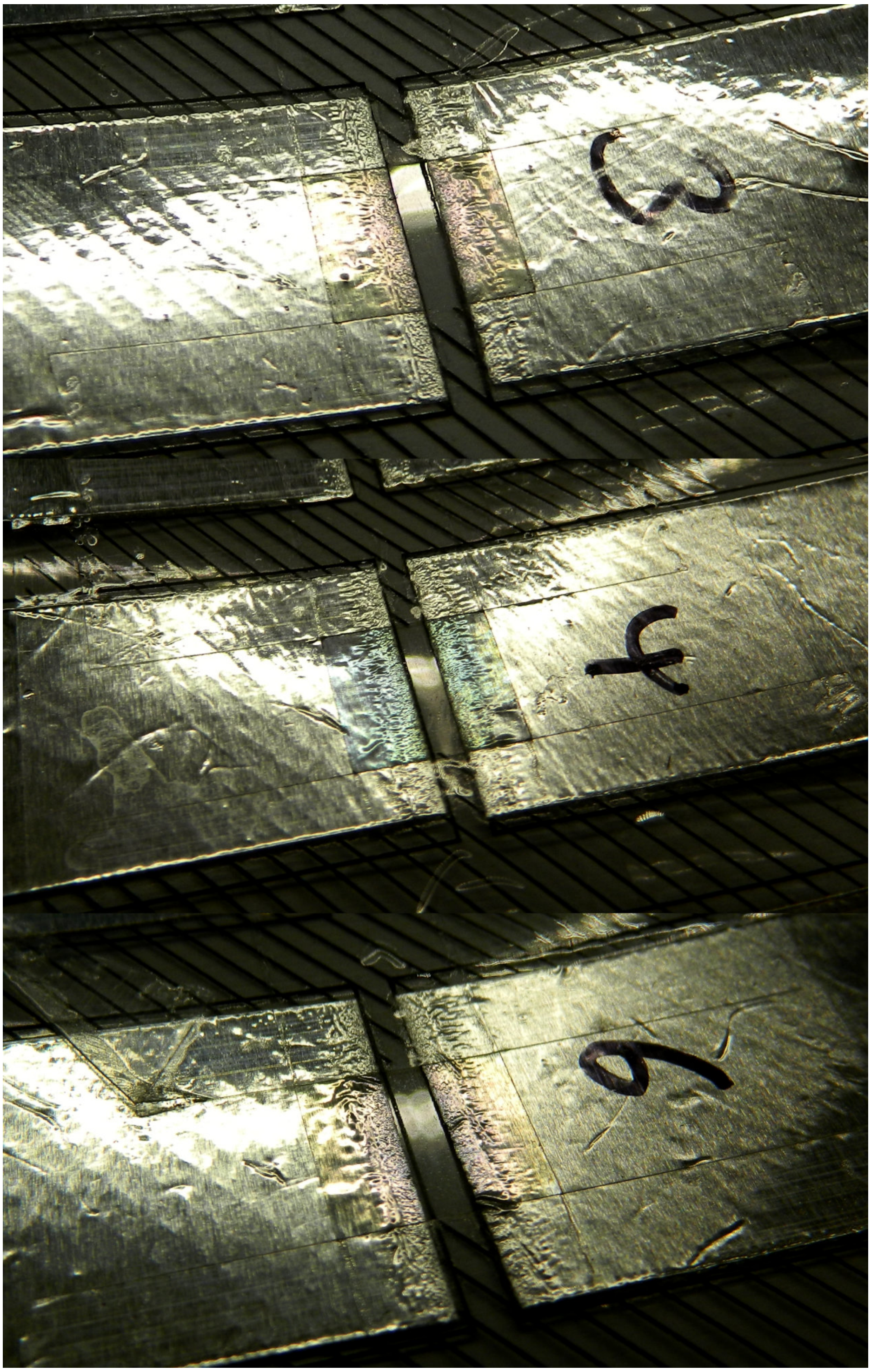


Figure 42: Various post-usage aluminium film colours. Only the central portions of the aluminium are exposed to the electrolyte during experimentation, the remaining parts are sealed by transparent sticky-tape.

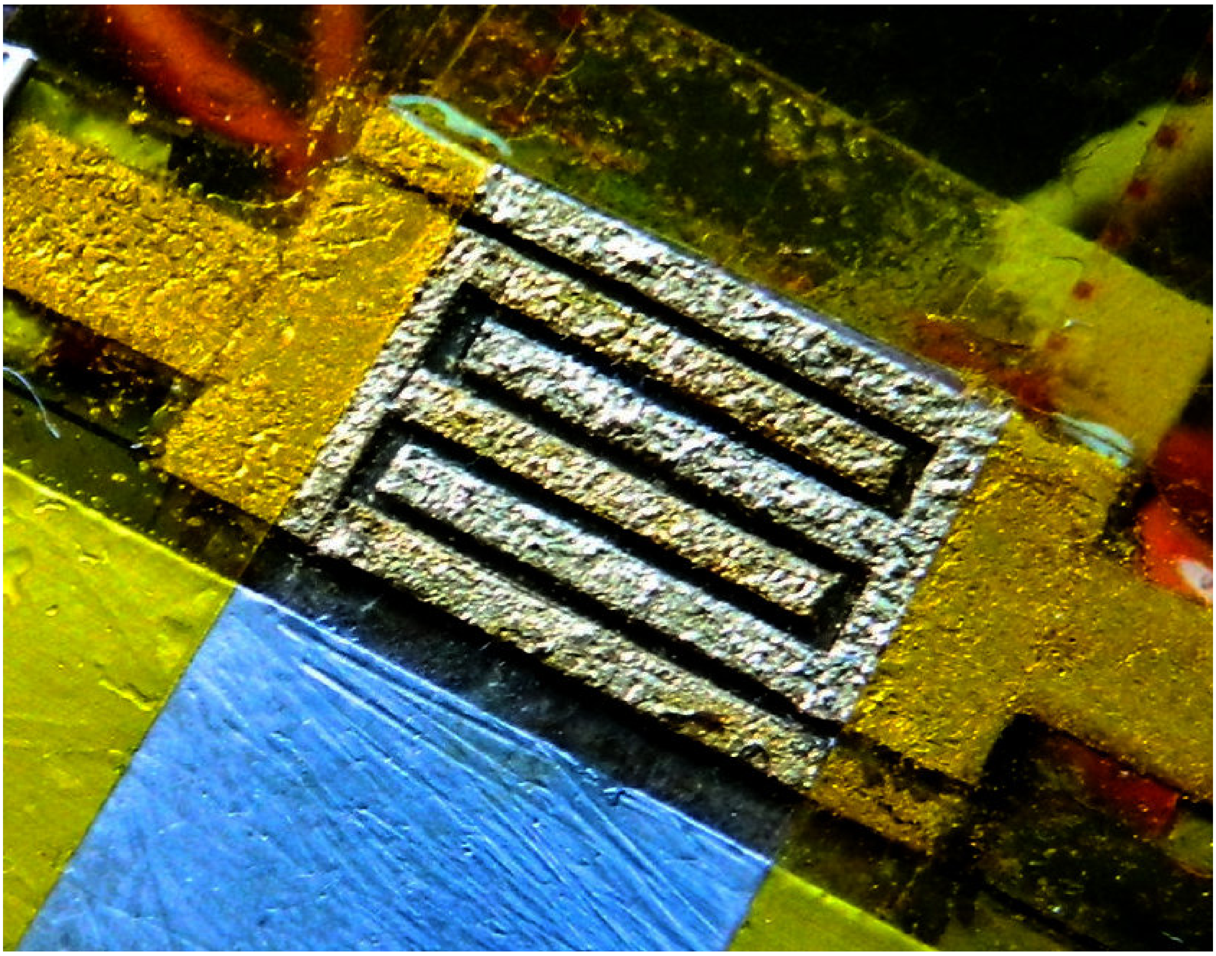


Figure 43: Interdigitated contacts with subtle colour differences

11 Further Detailed Experiments

11.1 (Part A) pH and air sensitivity of AERs

Aim To determine the effects of ingredient purity and air exposure on the performance of sodium carbonate aluminium ionic rectifiers.

Method The effects of *water purity* were tested by comparing AERs made using water from three sources:

- Ordinary home tapwater.
- "Deminerlised water" sold at a local hardware, with no specifications of purity on its label.
- $>$1Mohm per centimeter (cube resistance) de-ionised water from the UNSW Physics research laboratories.

The effects of *air exposure* were tested by mixing and storing electrolyte a few days prior to testing, then comparing its performance with freshly made electrolyte.

Performance was measured through two techniques:

1. AC curve tracing tests, using a circuit as described in section **??**.
2. DC resistance tests, where a multi-meter is used to measure the resistance of the AERs both forwards and backwards.

DC resistance tests are only applied for several seconds to avoid time-related experimental pitfalls. AERs typically increase their performance over time when a DC bias is applied (see section 4.1.1); but also dry out and reduce performance after several minutes.

Results The purity of the original water only weakly effects the performance and reliability of an AER. Distilled water AERs can be mixed and used almost immediately (after a several-minute settling delay) to create functioning devices whilst tapwater mixtures do not work reliably unless left to settle for at least one hour.

In either case, leaving the mixture sitting for 24 hours allows more reliable and better performing devices to be created. In AC tests poorly made devices exhibit uneven and unstable forwards behaviours as well as low reverse breakdown voltages (see figure 44). In DC tests poorly made devices have only a small resistance ratio between forwards and backwards conductance, typically less than a ratio of 5x.

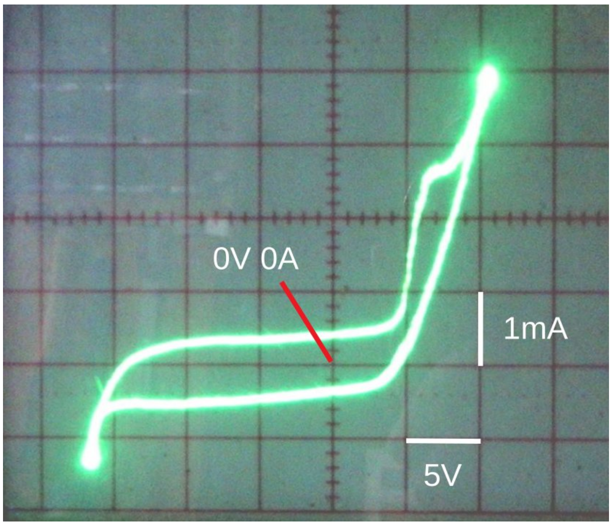


Figure 44: I-V curve trace of a poorly formed AER. Note the “loop” shape (capacitance/hysteresis) and uneven forward peak shape.

Well-settled electrolytes instead make better quality AERs, with AC performance as observed in previous tests such as figure 13 and DC resistance ratios of greater than 10x.

It was also observed that the pH of the electrolyte solutions changes very slightly over time when tested using litmus paper. All three water sources measured pH 6-7 initially, freshly mixed electrolytes measured approximately pH 8 and settled electrolyte mixtures (>24 hours) measured pH 9.

Discussion The small impact of water purity is not unexpected. The other ingredient (bicarbonate soda) used in the electrolyte preparation is cooking grade, not laboratory grade, so it is expected to have high levels of impurities. In dissolved solutions even small amounts of impurity can have high impact on electrical properties due to the high mobility of the dissolved ions. Using a pure ingredient in an otherwise impure system yields little benefits.

The ability of relatively impure ingredients to create functional devices is an extremely important outcome toward the goal of “low technology” devices accessible to average individuals. It demonstrates the resiliency of these devices to ingredient variation and contrasts them heavily to the highly-controlled processes necessary for traditional IC fabrication.

The pH change over such a small range is difficult to reliably measure and in practice took many repetitions of this experiment to confirm. This change hints at a changing internal chemistry.

It appears the “settling process” is a self-stabilising effect that converts the electrolyte into a more useful form. I theorise that atmospheric carbon dioxide is being slowly dissolved into the electrolyte and affecting the ionic balance inside the self-buffering chemistry (see section **??**). This simulates the effect of a powdered acid in "Baking Soda", as observed in section **??**. The exact reason how this improves device performance is unknown.

This experiment could be extended and improved by:

- Obtaining purer sodium bicarbonate and testing if that ingredient's purity affects results.
- Measuring a redox potential over time rather than a pH of the solution, as this may vary more and be easier to measure than the small pH change. A challenge would exist in avoiding this chemically affecting the solution.
- Repeat the experiment under a controlled (eg nitrogen) atmosphere to remove the affects of the atmosphere.
- Manually add a mild acid to the electrolyte to determine if the aging process can be sped up, and to confirm the acid's effects.
- Investigate how the dissolution of carbon dioxide could be associated with a raise in pH (make the solution more alkaline) in the buffered solution when dissolved carbon dioxide usually creates carbonic acid (lowering the pH).

12 Methodology Detail

It was noted that many published papers lack cruicial information needed to recreate described experiments. This section aims to counter-act this phenomena by providing advice on areas of particular difficulty or uniqueness.

12.1 Transferring and measuring very small quantities of electrolyte

12.1.1 Transferring

(1) Dip a standard drinking straw into a container of the electrolyte.

(2) Cover the top end of the straw with a finger

(3) Gently remove the straw.

A small amount of electrolyte will now be trapped in the tip of the straw. Removing your finger from the top will break the seal and allow the fluid to escape.

If the straw is always dipped to the same depth and this technique is practiced then a reasonably reliable volume of fluid (+/-10%) can be trapped with every attempt.

12.1.2 Measuring

Measuring small fluid volumes is extremely hard, however measuring fluid mass is not. Inexpensive scales purchased off the internet (<$10 AUD as of 2019) can measure down to 0.01 gram resolution.

12.2 Creating gold-leaf contacts

12.2.1 Preparing the adhesive and substrate

(1) Obtain thin double-sided tape. This will be used to stick the gold leaf onto your substrate of choice (eg over-head projectile slide plastic, or sticky-tape sealed paper).

This tape will be made of two layers: a wax-paper backer and a thin sticky polymer layer.

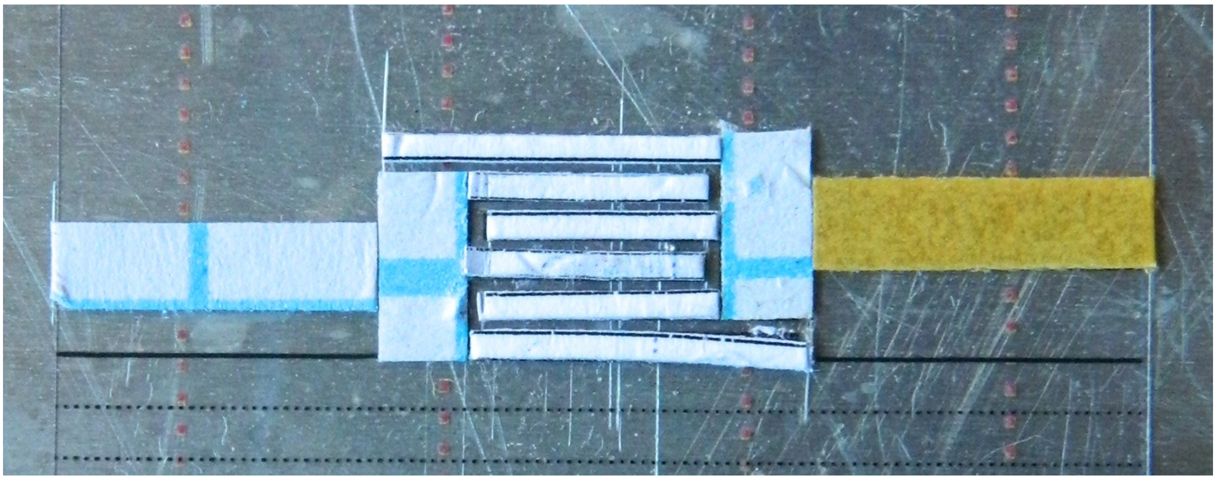
(2) Cut a section of this tape.

(3) Cover the sticky layer of this tape with a second layer of wax paper, so that a three-layer sandwich is made. This allows the tape to be handled and cut without interacting with the sticky layer.

Extra wax paper can be obtained by discarding some other tape or from rolls of book-cover contact.

12.2.2 Transferring the gold from book to substrate:

(1) Apply thin, double-sided tape to your substrate (eg sticky-tape sealed paper) in the pattern you wish the gold to appear in.



(2) Gently (partially) open the protective paper around a single piece of gold leaf. Only expose the amount you wish to use, and fold the paper back. Do not touch the leaf, you will destroy it.

(3) Place a flat bar of metal [21] (eg a flat knife-blade or a bar of aluminium) on the exposed gold leaf.

(4) Cut the leaf along the edge of this knife using a sharp blade. Use a stabbing motion to avoid "dragging" the gold.

(5) Gently lift the knife. The gold leaf should have adhered to it.

(6) Place the gilded knife onto the adhesive tape so that the gold touches the tape. The gold should transfer from knife to adhesive.

(7) Gently rub away excess gold using a toothbrush.

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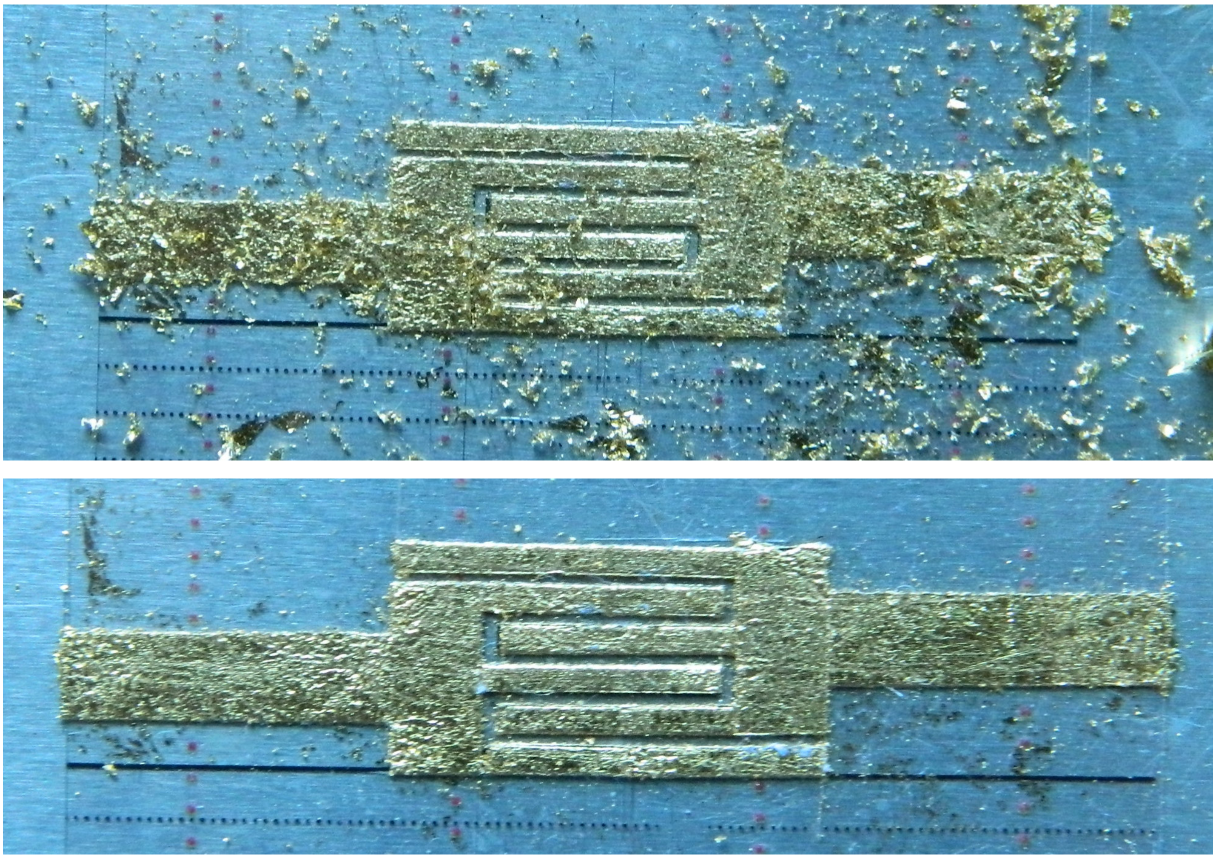
[21] This tool is commonly referred to as a 'gilding knife'.



(8) Test continuity of the laid-up gold. If it fails then apply more gold.

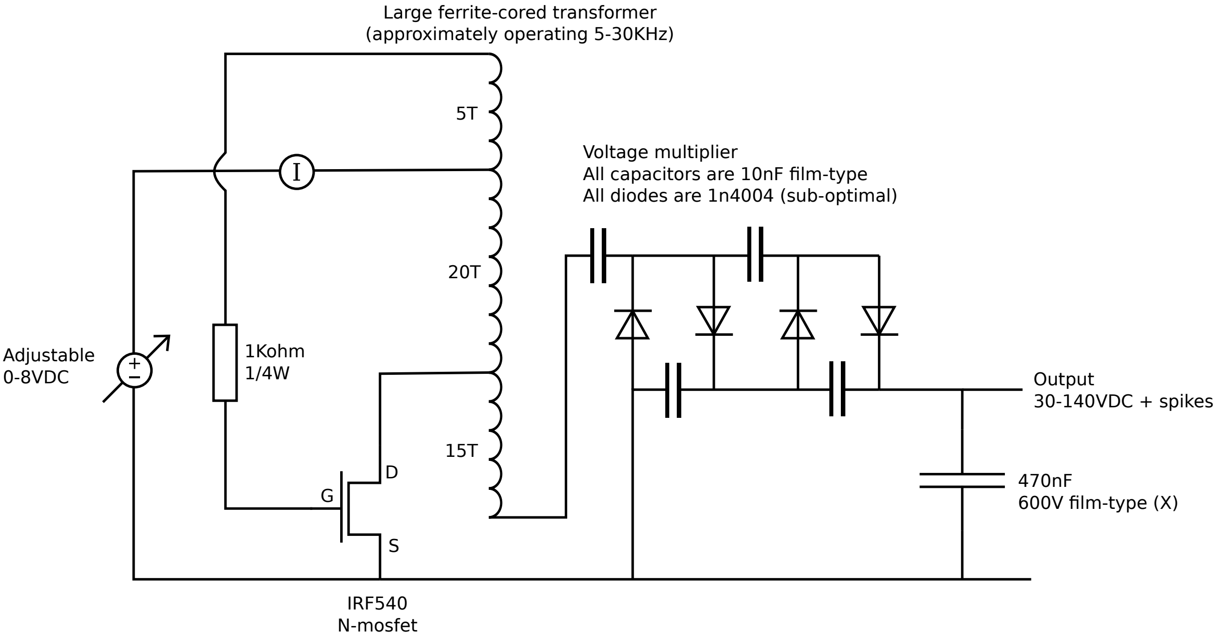
12.3 Simple joule-thief high-voltage DC supply

Whilst high DC voltages can be obtained through rectifying mains, it is generally safer to instead use a method that is intrinsically power-limited and isolated. A joule-thief style circuit (powered by an already isolated DC supply) is one option if a proper off-the-shelf supply is not available.

This circuit's ability to self-oscillate and its resulting performance are highly sensitive to the transformer, transformer taps and the exact switching device (eg mosfet model) used. Adjustment and experimentation of the transformer windings will be required depending on what parts you have available. Performance and efficiency depend on the drive voltage, ensure it is adjustable and that the current draw of the device is monitored (and limited) to avoid accidental damage.

I recommend using a fully-isolated DC supply to power this circuit and keeping experimentation similarly isolated from human-contact ground.

Do not construct this device if you do not understand the risks of high voltage and high-frequency circuits. Electrocution is a complex topic.


Large ferrite-cored transformer
(approximately operating 5-30KHz)
5T
20T
15T
I
Voltage multiplier
All capacitors are 10nF film-type
All diodes are 1n4004 (sub-optimal)
Adjustable
0-8VDC
+
−
1Kohm
1/4W
D
G
S
IRF540
N-mosfet
Output
30-140VDC + spikes
470nF
600V film-type (X)

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