

**THE PRODUCTION, APPLICATIONS AND ECONOMIC STUDY OF
ACTIVATED CARBON FOR LARGE SCALE PRODUCTION INCLUDING AN
EDUCATIONAL STUDY ON UNDERGRADUATE LABORATORY MODULES**

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MICHELLE JI

Dr. Galen Suppes, Thesis Advisor

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The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

THE PRODUCTION, APPLICATIONS AND ECONOMIC STUDY OF ACTIVATED
CARBON FOR LARGE SCALE PRODUCTION INCLUDING AN EDUCATIONAL
STUDY ON UNDERGRADUATE LABORATORY MODULES

presented by Michelle Ji,

a candidate for the degree of master of science,

and hereby certify that, in their opinion, it is worthy of acceptance.

Professor Galen Suppes

Professor Paul Chan

Professor Sheila Grant

...to the Chemical Engineering Department, University of Missouri.

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Disclaimer

This thesis includes estimates of equipment costs, operating costs, and profitability. These are only estimates prepared for discussion purposes. These estimates are not intended to represent an accurate assessment of the costs or profitability for any application.

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ABSTRACT

The production of activated carbon was evaluated using a biomass feed stock, corn cobs, as a precursor. The importance of the carbonization process and activation process are discussed and how nanopores and its unique surface chemistry allow activated carbon to perform advantageously in the transportation of natural gas. Adsorbed natural gas transportation is a valuable technique because of its ability to gain access and utilize methane from currently unavailable resources by conventional methods. A design approach was proposed and evaluated using the applications of activated carbon to transport natural gas including economic analyses on the large scale production of activated carbon.

In addition, an experimental learning module was developed to study the mass and energy balance involved with operation of an AA Alkaline battery under a load current. An extension of the module allows evaluation of laboratory assembled batteries using granular anodic/cathodic materials. The system allows load resistance to be varied and measures voltage and temperature. The importance of batteries and the integration of chemical engineering education is discussed involving the battery- resistor circuit module.

CHAPTER 1

THE CARBON PROJECT

1.1. Introduction of Natural Gas

Natural gas is a co-product of crude oil production and provides nearly one-fifth of all the world's primary energy requirements. It was discovered in Fredonia, New York in 1821, and initially it was used as fuel in areas immediately surrounding the gas fields. Since then, the construction of long -distance, large diameter pipelines have been able to bring the supply of gaseous fuel to domestic, commercial, and industrial consumers to areas miles away from the gas fields[1]. The turning point in the natural gas industry occurred after World War II due to increases in natural gas consumption for residential, commercial, industrial, and power generation. Several contributors led to this growth including the development of new markets, the replacement of coal, using natural gas in making petrochemicals and fertilizers, and the growing demand for low-sulfur fuels[2].

Natural gas is a mixture of hydrocarbons and other impurities. Methane is the main component in natural gas followed by ethane, propane, butane, pentanes, and small amounts of hexanes, heptanes, octanes, and other heavier gases[1]. The impurities present in natural gas include carbon dioxide, hydrogen sulfide, nitrogen, water vapor, and heavier hydrocarbons. The composition of natural gas varies from each stream, and each gas stream produced from a natural gas reservoir can change its composition as it is depleted[2]. The propane and heavier hydrocarbons are usually removed to be additionally processed because of their high market value, so the natural gas that is

available for consumers is mainly composed of a mixture of methane and ethane with a small percentage of propane.

The importance of natural gas has increased significantly in the last 25 years because of the widening infrastructure of pipelines and compressor stations that are being developed, especially transnational pipelines. Gas has also been established as an environmentally friendly fuel that burns much more efficiently than oil or coal. The only by-products released from natural gas if burned correctly are carbon dioxide and water. Natural gas is also sold at a discounted price in terms of energy equivalence since 6 MSCF (thousand standard cubic feet) of gas is equal to one barrel of oil. As a price comparison, 8-10 MSCF (thousand standard cubic feet) of gas is equivalent to one barrel of oil[2]. Natural gas is also being used as a motor fuel because it burns cleaner than traditional gasoline or diesel engines. Many vehicles are being retrofitted to use natural gas as an alternative to gasoline or diesel, and these engines are proving to be environmentally friendly and efficient[3].

There are currently two conventional types of natural gas storage and transportation in use, either in the form of liquefied natural gas or compressed natural gas. This chapter proposes an alternative method described as adsorbed natural gas using activated carbon to deliver natural gas that is unreachable by pipelines or other conventional methods. These gas fields are referred to as “stranded” natural gas either physically or economically. It is physically stranded because of its remote or geographically challenging location or economically stranded because the amount of gas produced is not sufficient enough to build a multi-million dollar facility for processing and distribution.

Adsorbed natural gas uses activated carbon, which is a highly adsorbent, nanoporous material to bind to the methane molecules, and the carbon is often referred to as a “sponge for natural gas[4].” Adsorbed natural gas is a viable alternative in natural gas storage and transport, and its economic feasibility including the large scale production of activated carbon is discussed in this chapter.

1.2. Types of Natural Gas Storage and Transportation

1.2.1. Liquefied Natural Gas (LNG)

The energy demands of Japan, Western Europe, and the United States were growing rapidly and could not be satisfied without importing natural gas. In the 1930s, the use of refrigeration to liquefy dry natural gas to reduce its volume was introduced in Hungary, and later used in the United States for moving gas from the gas fields in Louisiana to Chicago[1]. This liquefaction process became economically attractive to transport natural gas across oceans by tankers since the gas is reduced to about one six-hundredth of its original volume and the non-methane components are largely eliminated. Liquefied Natural Gas (LNG) technology also requires handling at very low temperatures around 108.15 K, and at the receiving terminals, LNG is reconverted into a gaseous phase using a regasifying plant and fed into the conventional gas distribution process of the importing country[5]. LNG can also be stored in insulated tanks or subsurface storages for future use. However, for LNG to be economically successful, certain parameters need to be satisfied. First, the location where the natural gas is produced should have reserves capable of producing 25 to 30 times the annual capacity of the plant. Second, as a rule of thumb, the cost of building a liquefaction plant ranges from \$225 to \$675 million for 100 MMSCFD (million standard cubic feet per day) capacity. Third, the tankers built for

LNG transportation requires special linings and double hulls. It is estimated that a 3 BCF (billion cubic feet) tanker costs \$260 million and transportation costs increase linearly with distance. And lastly, the LNG can only be distributed into specialized terminals, and the cost of re-gasification plants can run up to several hundred million dollars[2].

1.2.2. Compressed Natural Gas (CNG)

The major transportation of natural gas is carried through pipelines. On average, over 12,000 miles of new gas pipelines are completed per year within the last five to six years, most being transnational[2]. Currently, the main transportation of gas is carried out by using compressed natural gas. Compressed natural gas (CNG) can be used as a substitute for gasoline or diesel, and it is made by compressing natural gas to less than one percent of its volume at standard atmospheric pressure. It is stored and transported in heavy, thick-walled, cylindrical containers at pressures up to 3600 psig[6]. Another use for CNG is in internal combustion engines to power vehicles. CNG vehicles require more space for fuel storage than gasoline powered vehicles due to the physical properties of compressed gas, rather than a liquid like gasoline so there are challenges in creating space or maintaining free space in the construction of CNG vehicles[7]. Another consideration is the structural strength of the vehicle to withstand the heavy components of the storage tanks for compressed natural gas. The high cost of cylinders and the high pressure facilities limit the practical use of CNG in natural gas fuelled vehicles.

1.2.3. Adsorbed Natural Gas (ANG)

Adsorbed natural gas (ANG) provides a method of storing gas at a lower compression using activated carbon. It is a simpler process than liquefied natural gas or

compressed natural gas because it does not require the use of refrigeration or significant supplementary equipment. Activated carbon is a form of carbon that has been chemically processed in order to create a dense network of micropores and nanopores to increase its surface area for adsorption. The primary advantage of ANG technology over CNG is the low pressure. Activated carbon can be packed into storage vessels and filled with pressurized methane at 500 psig at ambient temperatures compared to 3600 psig for the CNG process[8]. Natural gas is attracted to the porous activated carbon by Van der Waals forces and later, the gas can be desorbed when subjected to higher temperatures or higher pressures[9]. This type of storage is appealing due to the fact that gas can be stored at lower pressures in a lower volume environment, which would be more convenient and economically efficient for transportation because it would use lighter, smaller tanks. Methane can be stored with relatively high energy density on activated carbon at ambient temperatures and low pressure (~500 psig), so the lower pressures would allow the use of larger containers for transportation to reduce the amount of wasted space and weight of the transport module[10].

For bulk storage applications, ANG technology is essentially dependent on the cost of the adsorbing material. However, the price of high performing carbons tends to increase disproportionately to the advantage gained in storage capacity[10]. For ANG applications, the capacity of the carbon is expressed as storage per unit volume in terms of volume per volume stored (v/v). Vigorous research efforts have been utilized to produce activated carbons capable of storing up to 190 volumes of gas per volume of storage space (v/v) at pressures of approximately 500 psig. The focus of this chapter will

be on the large scale production of activated carbon to transport stranded natural gas in the form of adsorbed natural gas (ANG).

1.3. Activated Carbon

1.3.1. Introduction

Activated carbon includes a wide range of processed amorphous carbon-based materials with a microcrystalline structure. They are known for their highly developed porosity and extensive surface area. Carbon is the major component of activated carbon and is present to the extent of 87 to 97%. Other elements are also present such as hydrogen, nitrogen, sulfur, and oxygen[11]. The most widely used activated carbon adsorbents have a specific surface area of 800 to 1500 m²g⁻¹ and a pore volume range of 0.20 to 0.60 cm³g⁻¹[9]. The surface area in activated carbons is primarily contained in micropores with effective diameters smaller than 2 nm. The pores in activated carbon can be represented by three groups: macropores with diameters greater than 50 nm, mesopores with diameters ranging from 2 to 50 nm, and micropores with diameters less than 2 nm[6]. The micropores encompass nearly 95% of the total surface area, thus they are considered to be the determining factor of the adsorption capacity of the activated carbon.

Activated carbon can be made from a wide variety of raw materials ranging from bones to coconut shells to wood; however, the properties of the finished activated carbon are greatly influenced by the source material and by the conditions of activation[12]. The preparation of activated carbon occurs in two fundamental steps: the carbonization process and the activation process. The carbonization process is performed at temperatures below 800 °C in an inert environment typically in the presence of nitrogen.

This process rids the carbonaceous material of noncarbon elements such as oxygen, hydrogen, and nitrogen using pyrolysis and forms a rudimentary porous structure as a precursor to the activation step[12]. Then the activation process is carried out using oxidizers in the temperature range of 800°C to 900°C to develop large internal surface areas as high as 3500m²g⁻¹[4]. The high surface area of activated carbon is crucial in its performance and adsorption capacity.

1.3.2. Activated Carbon and Adsorption

There are two types of adsorption depending on the nature of the forces involved: physical adsorption and chemisorption. Physical adsorption occurs when the adsorbate is bound to the surface by Van der Waals forces, and chemisorptions involves the exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent as a product of a chemical reaction[13]. In the case of activated carbon and natural gas, natural gas is adsorbed by physical adsorption by weak Van der Waals forces[14]. Many different parameters are significant in determining an accurate model for adsorption on activated carbon such as the concentration of the surface chemical groups, the surface area, the pore size distribution, and polarity of the surface[9].

1.3.3. Other Applications of Activated Carbon

Since activated carbons have exceptional adsorbing properties, they have gained important applications in the removal of color, odor, taste, and other undesirable pollutants from drinking water, in the treatment of waste water, and air purification[13]. There has been over 800 specific organic and inorganic chemicals identified in drinking water as a result from industrial discharge and chemical run off, from water chlorination

practices, and natural decomposition of plant and animal matter. Many of these chemicals are harmful and carcinogenic and activated carbon is essential in removing these dangerous components. Other uses for activated carbon also include applications in medicine and health to purify blood and to aid in the removal of certain toxins, and to purify pharmaceutical products and chemicals[15].

1.3.4. Activated Carbon Production

1.3.4.1. Materials and Experimental Procedure

Activated carbon is a nanoporous carbon material made from waste corn. One reason why corn is an attractive precursor is because of its abundance in Missouri in corn production, and it is Missouri's second largest production crop, producing nearly 460 million bushels annually[16]. Corn is used as the starting raw material because it is abundant, economically affordable, and environmentally conservative to produce activated carbon from waste material. Other materials have been used such as walnut shells and red oak, but they are more expensive to produce and lack a significant performance advantage compared to corn cobs.

Carbon is produced using a starting ingredient of Grit O' Cobs brand corn cobs provided by Anderson Farms. A 63:37 weight ratio of 85% Phosphoric Acid obtained from Fisher Scientific and de-ionized water is mixed thoroughly on a stir plate before it is added to the corn cobs. The acid/water mixture is added to the corn cobs in a stainless steel vessel using a 60:40 weight ratio of mixture to corn cobs. This hydrolysis process requires rigorous mixing because the acid needs to be distributed homogeneously to have the greatest affect on isolating the carbon product and removing all other volatile components[12]. After mixing, the product is transferred into a stainless steel vessel and

placed in a Fischer Scientific 750 series model 126 Isotemp Programmable Muffle furnace at 45°C for at least 12 hours. This is called the soaking process and this allows for the isolation of the carbon components, and to prepare it for the next reaction.

After the soaking process, nitrogen is introduced into the furnace at a purge rate of 5 L/min to create an inert environment and the corn cob mixture is placed in a fired heater at 380° C for 3 hours and then raised to 480° C for 2 hours. This is called the acid carbonization process or extreme pyrolysis and the resulting product is a carbon char. The char undergoes a washing process to remove any remaining acid, and then it is placed in a vacuum dryer to remove any moisture. A process flow diagram describing the production of activated carbon is shown in Figure 1-1.

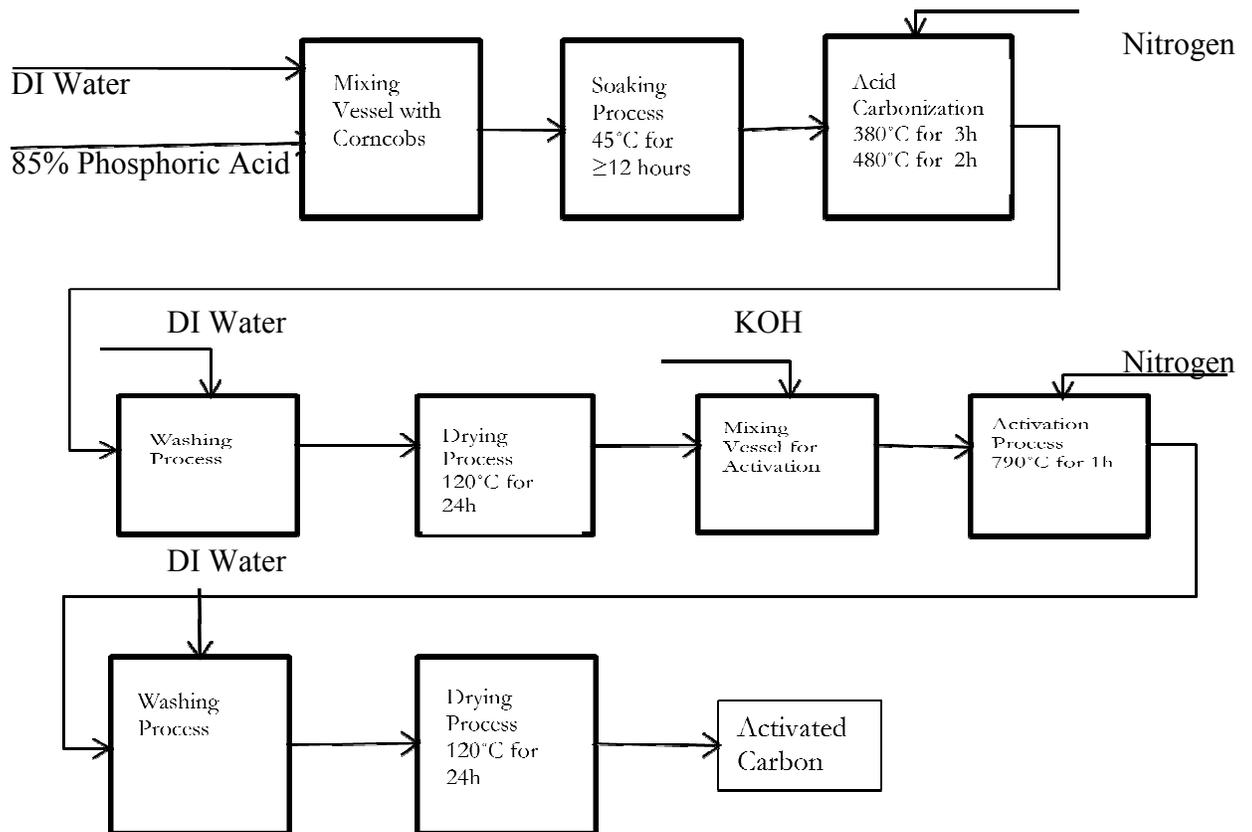


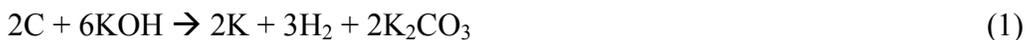
Figure 1-1 Block flow diagram of carbon production.

When the carbon is completely dry, it has an approximate mass loss of 60% from the initial corn cob mass. The char is ground into a fine powder using a Waring blender to a particle size of approximately 40 mesh, and mixed with potassium hydroxide (KOH) flakes (>90%) obtained from Sigma Aldrich. Adding a three to one ratio of KOH to the ground char has shown to be optimal in performance, verified in Table 1-1[17]. This is commonly noted as 3K carbon because the carbon is chemically activated with three times as much KOH. The chemically activated carbons depict a significantly higher surface area of over 2600 m²/g compared to the control sample with zero activation.

Table 1-1 Sample BET measurements for carbons. 3K Surface Area $\sigma=200$, 3K Porosity $\sigma=0.025$

Sample #	KOH Ratio	Process Temperature (°C)	Process Hold Time (hrs)	Specific Surface Area (m ² /g)
1	0	480	1	1150
2	2	790	1	1880
3	3	790	1	2670
4	4	790	1	2600

A small amount of water is added to form a thick slurry, starting the chemical activation, described by these two reactions[18]:



The mixture is placed into a nickel vessel because of its low corrosive properties and activated in a fired heater with nitrogen at 790° C for one hour. After the activation process, the carbon is washed with hot water in a Buchner Funnel to remove the K₂CO₃

formed and any residual KOH until a neutral pH was obtained. When the carbon is free of KOH, it is placed in a vacuum dryer to remove any remaining moisture. The result is the final activated carbon product.

1.3.5. Activated Carbon Mass Balance

Once the activated carbon is dry, it has a mass loss of approximately 70% of its starting char component so the overall yield is approximately 12% from corn cobs to activated carbon. The yield information is given in Table 1-2 shown below.

Table 1-2 Sample mass balance on activated carbon process: 3K, 790°C, 1 hour

Mass Corncob Feedstock	1000 g
Mass Carbon After Phosphoric Acid Carbonization, Washing, Drying	417 g
Sample Mass Loss in Phosphoric Acid Carbonization	58.3%
Mass Carbon Used in KOH Activation	417 g
Sample Mass Loss in KOH Activation	11.1%
Mass Carbon after KOH Activation, Washing, Drying	119 g
Mass Loss in KOH Activation	71.4%
Overall Process Yield Corncob to 3K Carbon	11.9%

This sample mass balance on activated carbon shows a 58.3% mass loss due to the acid carbonization process and a 71.4% mass loss in the chemical activation process using KOH, giving a resultant yield of 11.9% of activated carbon from the initial raw corn cob material. The mass loss that occurs during the acid carbonization step is due to

the removal of non carbon elements in corncobs such as water and carbon dioxide. It is reasonable to have a 60 % mass loss during the acid carbonization process because corn cobs are comprised of approximately 43.5% carbon, thus the remaining carbon[6]. The mass loss that occurs during the chemical activation step is due to the micropores being formed within the network of dense pores already present, increasing its surface area and adsorption capacity.

1.4. Adsorbed Natural Gas Progress and Goals

Adsorbed Natural Gas technology has numerous environmental and energy conservation applications. Using ANG technology to transport stranded natural gas could reduce dependence on foreign oil, increase domestic renewable energy resources, and create new opportunities for domestic agriculture and waste management. Presently, the majority of natural gas is obtained from domestic (85%) and Canadian fields, with research in progress to achieve renewable methane from landfills and biomass feed stock[2]. Future goals include technology to safely and efficiently obtain methane from deep-sea methane hydrate fields.

1.5. Introduction to Economical Analysis

1.5.1. Base Case Scenario

This project focuses on the large scale production of activated carbon to transport stranded natural gas. The base case requirements of this project are as follows:

- To produce 2000 pounds of activated carbon/ day
- Well head producing 160,000 SCF crude natural gas/ day
- 500 miles distance from well head to distribution site

- ANG containers loaded on semi- trucks (8ft x 13.5ft x 53ft)
- Carbon packing density of 0.5g/cm³

1.5.2. Large Scale Carbon Production

1.5.2.1. Cost of Materials and Size of Equipment

For the production of 2000 lbs/day of activated carbon, Table 1-3 summarizes the quantity of materials needed per day using the ratios described earlier.

Table 1-3 Materials for the production of 2000 lbs/day of activated carbon.

To produce 2000 lb of activated carbon		
Materials	Amount (lb)	Ratio
Grit O' Cob Corncobs	16700	40:60 Corn: Acid mixture
85% Phosphoric Acid	15750	63:37 Acid: Water
DI Water	9250	
Approximate Char remaining	6670	Assume 60% mass loss Char
KOH	20000	
Approximate AC remaining	2000	Assume 70% mass loss

Using cost estimates from Chemical Marketing Reporter, the daily and annual cost summaries are listed in Table 1-4.

Table 1-4 Cost estimation for the production of 2000 lbs/day of activated carbon.

Materials/ Chemicals	Units of Issue	Quantity Needed	Unit Price (\$)	Daily Cost (\$)	Annual Cost (\$)
Grit O' COB Corncob	40 lbs	417	17	7,089.00	2,480,000
o-Phosphoric Acid, 85% (Certified ACS)	100 lbs	158	36.20	5,719.60	2,000,000
KOH Flakes	25 kg	363	65.00	23,595.00	8,260,000
			TOTAL	36,400.00	12,700,000

A simplified process flow diagram was constructed for large scale production of activated carbon shown in Figure 1-2 and the list of equipment is shown in Table 1-5.

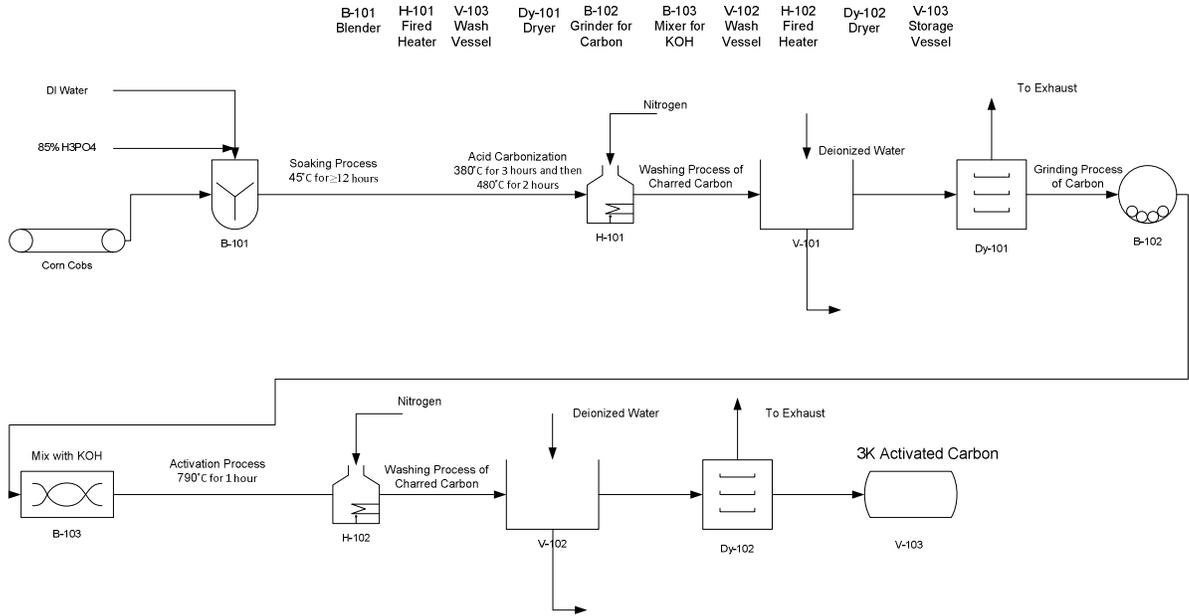


Figure 1-2 Process flow diagram of activated carbon production.

Table 1-5 List of equipment used for activated carbon production.

Block	Unit Operations
B-101	Blender
B-102	Grinder for Carbon
B-103	Blender for Activation
Dy-101	Dryer
Dy-102	Dryer
H-101	Furnace for Acid Carbonization
H-102	Furnace for Activation
V-101	Wash Vessel
V-102	Wash Vessel
V-103	Storage Vessel

The cost and size of equipment needed for producing 2000 lbs of activated carbon is summarized in Table 1-6 using the CapCost 2008 program without recycle.

Table 1-6 Cost and size of equipment for carbon production without recycle.

Materials	
Type	Yearly
Corn Cobs	\$ 2,480,000
H ₃ PO ₄	\$ 2,000,000
KOH	\$ 8,260,000
Total	\$12,740,000

Utilities	
Type	Yearly
Electricity	\$ 636,000
Natural Gas	\$ 700,000

Blenders & Grinders

Unit	Type	Volume (ft ³)	Base Cost	BMC
B-101	Rotary	1250.00	\$ 236,000	\$ 354,000
B-102	Rotary	618.00	\$ 117,000	\$ 176,000
B-103	Rotary	1020.00	\$ 185,000	\$ 278,000

Dryers

Unit	Type	Area (ft ²)	Base Cost	BMC
Dy-101	Rotary	618.00	\$ 268,000	\$ 402,000
Dy-102	Rotary	306.00	\$ 146,000	\$ 219,000

Furnaces

Unit	Type	MOC	Heat Duty (MJ/h)	Base Cost	BMC
H-101	Fired Heater	CS	3210	\$ 664,000	\$ 1,410,000
H-102	Fired Heater	CS	3610	\$ 664,000	\$ 1,410,000

Vessels

Unit	Type	MOC	Diameter (ft)	Length/Height (ft)	Base Cost	BMC
V-101	Horizontal	Nickel	8.69	26.08	\$ 37,000	\$ 453,000
V-102	Horizontal	CS	7.56	22.69	\$ 28,100	\$ 84,600
V-103	Horizontal	CS	7.56	22.69	\$ 28,100	\$ 84,600

1.5.2.2. Annual Operating Costs

The annual utilities cost summary is shown in Table 1-7 broken down by equipment type and form of utility used. Rough estimates (not recommended for design) of the utilities were estimated as follows:

Table 1-7 Annual utilities cost summary of equipment used for carbon production.

Name	Total Module Cost	Grass Roots Cost	Utility Used	Efficiency	Actual Usage	Annual Utility Cost
B-101	\$ 418,000	\$ 536,000	NA			
B-102	\$ 208,000	\$ 267,000	NA			
B-103	\$ 327,000	\$ 420,000	NA			
Dy-101	\$ 474,000	\$ 608,000	Electricity		2270 MJ/h	\$ 317,800
Dy-102	\$ 258,000	\$ 331,000	Electricity		2270 MJ/h	\$ 317,800
H-101	\$ 1,670,000	\$ 2,380,000	Natural Gas	0.9	3570 MJ/h	\$ 329,500
H-102	\$ 1,670,000	\$ 2,380,000	Natural Gas	0.9	4010 MJ/h	\$ 370,500
V-101	\$ 534,000	\$ 590,000	NA			
V-102	\$ 100,000	\$ 142,000	NA			
V-103	\$ 100,000	\$ 142,000	NA			
Totals	\$ 5,800,000	\$ 7,800,000				\$ 1,340,000

An equivalent annual operating cost was formulated in Table 1-8 using equations found in Turton *et al*[19], taking into account capital cost, and estimated equipment life.

Table 1-8 Equivalent annual operating cost for carbon production.

Discount rate =	0.1			
Equipment	Capital Cost	Operating Cost (per year)	Equipment Life (year)	Equivalent Annual Operating Cost (EAOC)
B-101	\$ 536,000.00	\$ 52,900.00	10	\$ 140,000.00
B-102	\$ 267,000.00	\$ 52,900.00	10	\$ 96,400.00
B-103	\$ 420,000.00	\$ 52,900.00	10	\$ 121,000.00
H-101	\$ 2,380,000.00	\$ 329,500.00	10	\$ 717,000.00
H-102	\$ 2,380,000.00	\$ 370,500.00	10	\$ 758,000.00
Dy-101	\$ 608,000.00	\$ 317,800.00	10	\$ 417,000.00
Dy-102	\$ 331,000.00	\$ 317,800.00	10	\$ 372,000.00
V-101	\$ 590,000.00	\$ -	10	\$ 96,000.00
V-102	\$ 142,000.00	\$ -	10	\$ 23,100.00

V-103	\$ 142,000.00	\$ -	10	\$ 23,100.00
			Total EAOC=	\$ 2,760,000.00
*EAOC= (Capital investment)(A/P,I,neq) +(YOC)				

The total summary of purchase costs is summarized in Table 1-9 broken down by equipment type. The bare module cost is the summation of the bare equipment cost, adjustment factors for design pressure, materials of construction, and equipment setting[19]. And the grass roots cost refers to the cost of manufacturing the equipment and building a completely new facility which is calculated by multiplying the bare module cost by a factor of 1.68.

Table 1-9 Summary of total purchase costs of process equipment by equipment type.

Equipment	Bare Module Cost	Grass Roots Cost
Fired Heaters	\$ 2,820,000	\$ 4,760,000
Blenders	\$ 808,000	\$ 1,223,000
Dryers	\$ 621,000	\$ 939,000
Vessels	\$ 622,200	\$ 874,000
Total	\$ 4,870,000	\$ 7,800,000

1.5.2.3. Net Present Value Over Ten Years

Taking into account the total initial investment needed for an annual production of Activated Carbon, a net present value spreadsheet was created to analyze incoming and outgoing cash flow, to appraise this project on a long term basis, and to provide an initial foundation for capital budgeting[19]. The price of activated carbon calculated for a net present value of zero during a period of ten years is shown in Table 1-10 below. The initial investment includes the \$7.8 million equipment cost with an additional ten percent of the annual material cost, resulting in \$9.85 million. The cost of manufacturing

includes the \$12.7 million in raw material costs with utility costs, resulting in \$14.04 million. The net present value calculation also incorporates a ten percent interest rate and a 42% tax rate per year. The price of the carbon to break even in ten years is shown below.

Table 1-10 Net Present Value calculations for the production of activated carbon (without recycle) in millions of dollars.

i(p.a.)= 0.1		WC(at the end of year 2)= 2.89		t= 0.42 /year		S= 0				
C _I = 1.25		FCI _I = 9.85		5.5 year MACRS						
End Of Year	Investment	R	COM _d	Cashflow	CCF	d _k	After-tax Profit	After-tax Cash Flow	DCF	DCCF
0	-9.85	0.00	0.00	-9.85	-9.85	0.00	0.00	-21.80	-21.80	-21.80
1	0.00	20.01	14.04	5.97	-3.88	1.97	2.32	4.29	3.90	-17.90
2	0.00	20.01	14.04	5.97	2.09	3.15	1.63	4.79	3.96	-13.94
3	0.00	20.01	14.04	5.97	8.06	1.89	2.37	4.26	3.20	-10.75
4	0.00	20.01	14.04	5.97	14.03	1.13	2.80	3.94	2.69	-8.06
5	0.00	20.01	14.04	5.97	20.00	1.13	2.80	3.94	2.45	-5.61
6	0.00	20.01	14.04	5.97	25.97	0.57	3.13	3.70	2.09	-3.52
7	0.00	20.01	14.04	5.97	31.94	0.00	3.46	3.46	1.78	-1.75
8	0.00	20.01	14.04	5.97	37.90	0.00	3.46	3.46	1.62	-0.13
9	0.00	20.01	14.04	5.97	43.87	0.00	3.46	3.46	1.47	1.34
10	1.25	20.01	14.04	7.22	51.09	0.00	3.46	-3.46	-1.33	0.00
								NPV=	0.00	
Rev/Year=				20.01	million					
Carbon Produced =				2000	lbs/day					
Carbon/year*=				700000	lbs/year					
Cost of carbon needed to break even=				\$ 28.58	per lb					
* Assumes 350 days/year for maintenance and holidays										

1.5.2.4. Cost of Carbon Production with 70% Recycle

With an initial investment of \$9.85 million and an annual cost of manufacturing of \$14.04 million which includes materials and utilities, an annual revenue of \$20.01

million has to be generated, the cost of activated carbon is calculated to be \$28.58 per pound to break even over ten years. This price is considered to be noticeably higher compared to commercial products, however, after a separate computation allowing for a 70% recycle of chemicals used provided by Aspen software, the materials and equipment cost was dramatically decreased shown in Table 1-11.

Table 1-11 Cost and size of equipment for carbon production with 70% recycle.

Materials	
Type	Yearly
Corn Cobs	\$ 2,456,000
H ₃ PO ₄	\$ 590,000
KOH	\$ 2,497,000
Total	\$5,543,000

Utilities	
Type	Yearly
Electricity	\$ 60,820
Natural Gas	\$ 700,000

Blenders & Grinders

Unit	Type	Volume (ft³)	Base Cost	BMC
B-101	Rotary	26.68	\$ 178,000	\$ 266,000
G-101	Rotary	27.76	\$ 181,000	\$ 272,000
G-102	Rotary	22.24	\$ 162,000	\$ 242,000

Dryers

Unit	Type	Area (ft²)	Base Cost	BMC
Dy-101	Rotary	38.32	\$ 28,300	\$ 42,400
Dy-102	Rotary	17.55	\$ 28,300	\$ 42,400

Furnaces

Unit	Type	MOC	Heat Duty (MJ/h)	Base Cost	BMC
H-101	Pyrolysis	Nickel	3210	\$ 462,000	\$ 1,300,000
H-102	Activation	Nickel	3610	\$ 555,000	\$ 1,560,000

Vessels

Unit	Type	MOC	Diameter (ft)	Length/Height (ft)	Base Cost	BMC
V-101	Horizontal	Nickel Clad	8.16	24.47	\$ 32,600	\$ 228,000
V-102	Horizontal	CS	7.51	22.57	\$ 27,800	\$ 83,600
V-103	Horizontal	CS	8.11	24.32	\$ 32,200	\$ 96,800

1.6. Conclusion

Adsorbed natural gas technology provides a safe and environmentally friendly alternative in fuel storage requiring simple compression, low pressure, and low temperature surroundings. The production of extremely high porosity carbons have been engineered for bulk storage natural gas vehicle applications.

The economics of activated carbon production relies heavily on product yield and method of activation. Implementing a 70% recycle on the use of phosphoric acid and potassium hydroxide plays a significant role in decreasing the price of carbon. These economics are also considerably affected by selling the activated carbon in a price based on its adsorption capacity and not on its weight[20] since its performance is substantially better than commercial products currently in the market. Calculating the plant capacity at its break-even point and conducting a sensitivity analysis would allow for future studies in optimization and minimizing the cost of production to provide a greater incentive for profit.

CHAPTER 2

INTRODUCTION OF BATTERY MODULE

2.1 Importance of Battery Technology and Introduction of Modules

The chemical engineering field of study is undergoing changes with goals of introducing design earlier in the curriculum and increasing utilization of experiential learning throughout the curriculum.[21] A modular battery experiment has been developed and used in a sophomore-level mass and energy balance course and a junior-level measurements lab toward these goals. These experiments assess the student's ability to use the techniques, skills, and modern engineering tools necessary for engineering practice, and it also allows them to demonstrate their ability to design and conduct experiments, and to analyze and interpret data.[22]

An additional goal of this module is to introduce chemical engineering students to battery technology since batteries will play the pivotal role in energy security of modern societies. As an alternative to petroleum, batteries can be used in hybrid electric vehicles (HEVs) and plug-in HEVs to displace petroleum and increase the efficiency with which limited petroleum resources are consumed. Alkaline manganese–zinc batteries are the most convenient primary batteries as the source of power for portable electronic and electric appliances.[23] For advanced devices, alkaline MnO_2 –Zn batteries are preferred, which use electrolytic manganese dioxide (EMD) and an alkaline electrolyte (KOH).[24] When used with the electric grid, batteries are able to enhance technologies related to wind power, solar power, and peak load shifting.[25] These topics provide students with

exceptional platforms to which they can relate their investigations to contemporary issues.

The battery- resistor circuit module allows heat transfer, mass transfer, reactions, circuit theory, heat/mass balances, and product design to be studied in a single module. The module also provides a good preparation for the study of sensors, biosensors, and instrumentation because of its integrated approach using MATLAB, LabVIEW data acquisition systems, and virtual instruments, which incorporates different aspects of the engineering curriculum. Once the standardized workstations, stands, and storage are in place, individual modules can be produced for a few hundred dollars with four modules occupying about two square feet of space when stored in the storage cabinet.

The importance and utilization of battery technology has exponentially increased in the last 20 years with the widespread introduction of hybrid electric vehicles (HEVs), and society's consciousness of using renewable resources and alternative energy. Due to more rigorous environmental regulations, battery technology is a fundamental element to initialize resource preservation efforts. Students will gain a practical laboratory experience which incorporates theoretical modeling and real world applications of batteries.

2.2 Objectives

- To develop experiments using the battery-resistor circuit module for the University of Missouri – Department of Chemical Engineering within the Mass and Energy Balance, Unit Operations, and Process Measurements courses
- To demonstrate fundamental concepts using modeling and simulations in a battery-resistor circuit

- To introduce Laboratory Virtual Instrumentation Engineering Workbench (LabVIEW) software and its integration with the undergraduate laboratory modules
- To create Portable Document Format (PDF) files which demonstrate modular use and software use for future students

2.3 Energy Balance for Battery-Resistor Circuit Module Description

The Energy Balance for Battery-Resistor Circuit module is shown in Figure 2-1 comprised of circuitry mounted on a 1 cm thick Lexan panel.

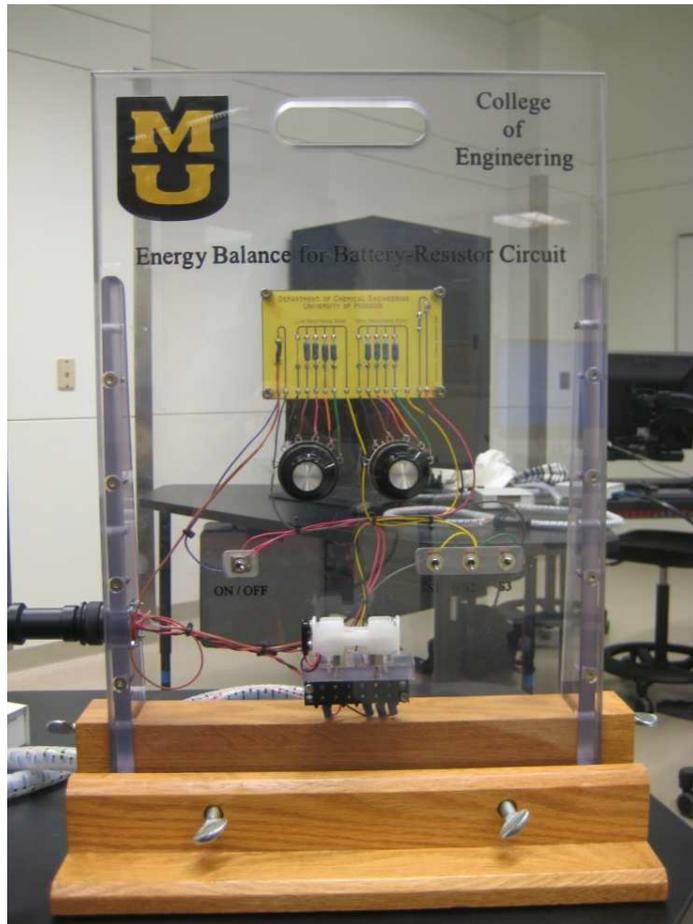


Figure 2-1 Energy Balance for Battery-Resistor Circuit module.

The module consists of a resistor bank with several different settings and selector knobs to control the total resistance applied to the battery, and switches to control where the voltage is measured. The front panel also shows an AA battery holder that can also be converted to connect to unconventional batteries made in the laboratory, and a data acquisition cable connected to the module.

2.3.1. Storage Capabilities and Equipment

The panel and re-enforcing bases are mounted on an oak base. A cabinet allows compact storage of sixteen modules and mounting bases shown in Figure 2-2.



Figure 2-2 Storage cabinet for stand-alone laboratory modules.

Each module connects to a computer workstation equipped with a National Instruments data acquisition card: NI PCI-6259, a shielded connector block: NI SCB-68 and LabVIEW 8.6 software. Use of a standardized 24-pin connector allows different experiments to use the same connector interface and respective workstation.

2.3.2. Description of Hardware and Circuitry

Figure 2-3 provides close up images of the AA battery connector, resistor bank, and voltages switches. A small thermocouple embedded in the AA battery holder monitors the battery temperature, which is used for the energy balance.

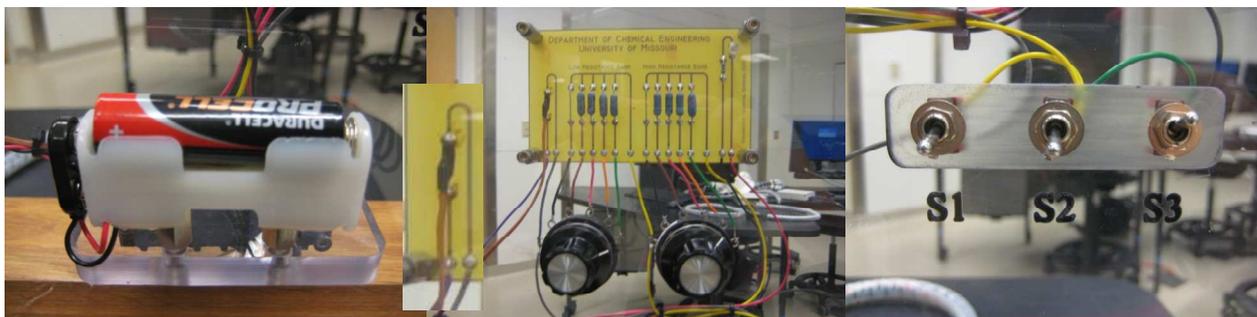


Figure 2-3 Close up images of module, including from left to right: AA battery holder; expanded image of 1-ohm resistor with thermocouple attached with shrink wrap; circuit board with 1-ohm resistor, two resistor banks, and knobs for selecting resistance from two resistor banks; and switches used to select locations for voltage measurements.

A second thermocouple is attached to the 1-ohm resistor—the temperature profile of the 1-ohm resistor is the key measurement for the energy balance studies. The 1-ohm resistor is connected in series with two other resistors from two resistor banks as selected by the selector-switches. Each selector switch has five settings allowing 25 different loads to be measured. The left selector switch has resistor settings 0, 1, 2, 3, and 5 ohms, and the right selector switch has resistor settings 0, 5, 10, 20, and 30 ohms depicted by

Figure 2-4. These resistor banks allow variations in an assignment to be made so no two groups or individuals have the same exact experiment. This allows the students to compare their data with other individuals or groups to relate the effect of the changes in resistor load, promoting a more interactive learning environment.[26]

2.3.3. Schematic of Resistor Bank

A series of three switches allow students to measure voltages at different locations in the circuit. Figure 2-4 provides a schematic of the two resistor banks with the two associated selector-switches, and the three switches that allow voltages to be measured over the different loads. The first resistor bank consists of resistors 0, 1, 2, 3, and 5 ohms, and the second bank consists of resistors 0, 5, 10, 20, and 30 ohms.

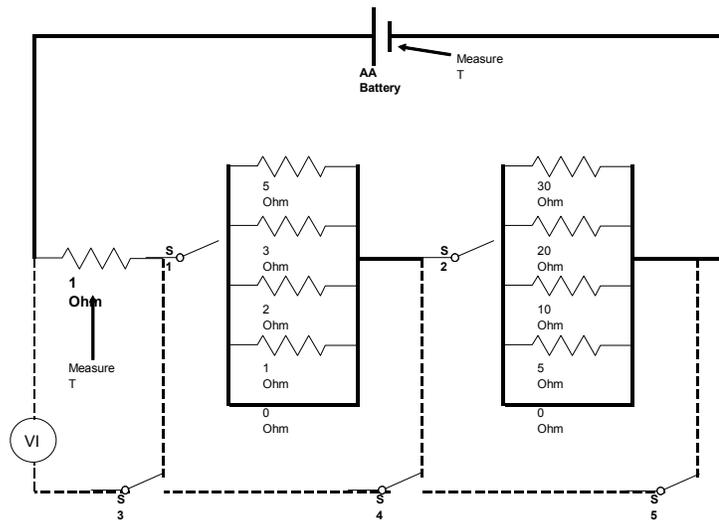


Figure 2-4 Schematic of the experimental system which shows the different resistors in series and switch settings for voltage measurements.

2.4 Data Acquisition Software

The LabVIEW program BatteryResistorEnergyBalance.VI is for the acquisition of voltage profiles, and temperature profiles of the battery and 1-ohm resistor. LabVIEW is installed on Dell workstation running on the Windows 7 operating system.

2.5 LabVIEW BatteryResistorEnergyBalance.VI Program Explanation

Figure 2-5 shows the front panel of the BatteryResistorEnergyBalance.VI program which records voltage, resistor temperature, and battery temperature as a function of time. Data files created by LabVIEW are readily accessible by MS Excel and include columns of time, resistor temperature, battery temperature, and voltage (as selected by the switch settings). The first time the experiment is run by a group, it takes about 25 minutes. Subsequent runs take about 10-15 minutes.

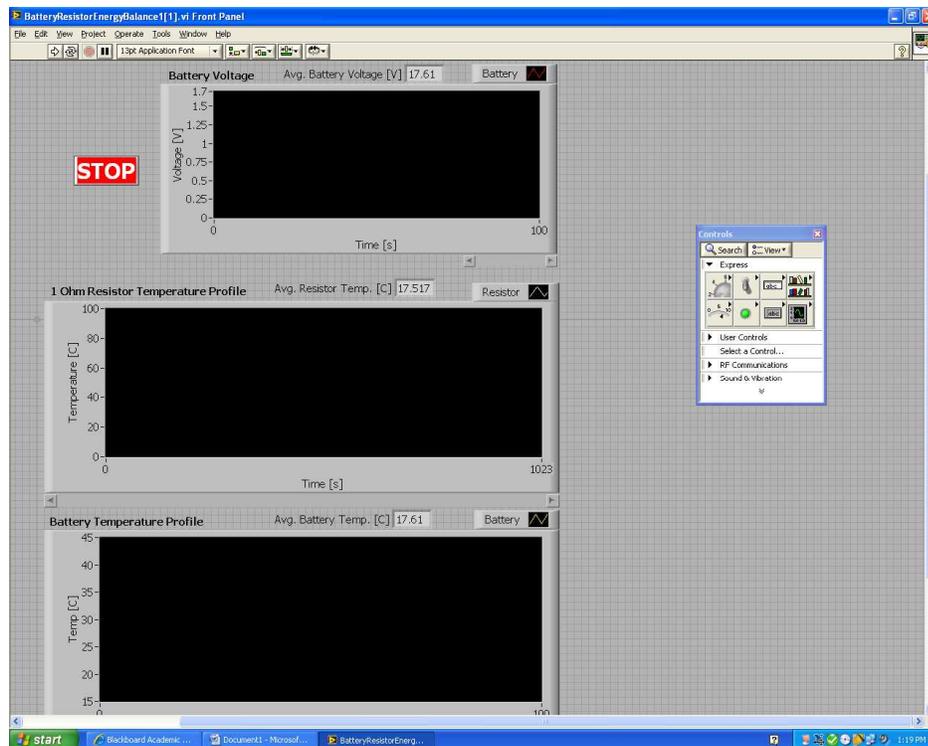


Figure 2-5 Front panel view of LabVIEW BatteryResistorEnergyBalance.VI program.

The data display boxes on top of each graph show battery voltage in Volts, and temperatures in degrees Celsius. The white “run” arrow at the top left of the screen will prompt the user to indicate a location for the data file created by LabVIEW, and this will also cause the program to initiate and start recording data.

2.6 Operating Procedures

Operating the module consists of the following steps:

1. Insert and fasten the module on a base at a workstation and connecting the 24-pin connector that connects the module to the National Instruments based data acquisition system.
2. Place AA battery in the battery holder or connect ancillary battery to system.
3. Start module-specific LabVIEW virtual instrument file (VI).
4. Set module selector switches (N1 and N2) to provide experiment-specific resistance, put S1 and S2 in the down position and S3 in the up position to measure voltage across entire load.
5. Toggle the run arrow button on LabVIEW VI followed by switching the module on using the module’s on/off switch.
6. Record data for the desired time (typically 5-10 minutes) and then click on the LabVIEW VI “STOP” button.
7. Return module switch to the off position and either repeat or disassemble the experiment.
8. Now the apparatus is ready for experimentation.

CHAPTER 3

LABORATORY TEACHING MODULES

3.1 Introduction

These laboratory experiments can be used to develop fundamentals in engineering on different educational levels in the undergraduate chemical engineering curriculum. The students will apply practical skills such as modeling, simulations, and evaluations of a dynamic model using both analytical and visual proficiencies. Three different experiment-based projects can be performed using this module as follows:

- Battery Resistor Energy Balance
- Evaluating the Internal Resistance of a Battery
- Diffusion and Permeability in Manganese Dioxide-Zinc Battery

3.2 Project 1: Battery Resistor Energy Balance

The purpose of Mass and Energy Balance Experiment is to predict and then model the transient temperature profile of the 1-ohm resistor that is connected in series with two resistor banks and an AA battery. The students are also to develop applications to measure and record temperature, voltage, current, and concentration of mass as a function of time. Virtual instruments will be used to simulate different systems by the use of various resistors and experimental data will be modeled as a function of time to describe how the battery and resistor work in a circuit.

The students are given minimal guidance in the initial prediction of the temperature profile beyond a schematic of the circuit, knob settings, and the specification of the brand name and type (zinc-alkaline) of battery.

Objectives:

- To use the Energy Balance for Battery-Resistor Circuit Module for applications in the design of more efficient alkaline batteries
- To specify the design of the smallest alkaline battery capable of powering a 10W light bulb for a period of one hour, using the same materials and chemistry as the Duracell Procell Battery provided
- To understand how the battery and resistor function in a circuit over time, and to extrapolate the information obtained to design a larger battery to power the light bulb
- To perform simulations, preliminary and primary experimental measurements of the system as well as modeling of the experimental data using Matlab and different analytical approaches

3.2.1 Laboratory Operational Procedures

Procedure Set- Up	Principle
<p>I. Operational Procedures</p> <ol style="list-style-type: none"> 1. Obtain a circuit board and a base holder, noting the Module number 2. Insert the circuit board into the base and tighten the screws on the sides of the base holder first, and then loosely tighten the screws in front to prevent the glass from cracking 3. Make sure that the board is OFF before the battery is loaded, and insert the data 	<p><i>(It is best to use the same board for all data to decrease discrepancies)</i></p> <p><i>(This will make sure that the battery does not drain)</i></p>

<p>acquisition cable into the side of the board</p>	
<p>II. Operational Procedures</p> <ol style="list-style-type: none"> 1. The switch configurations should be S1 down, S2 down, and S3 up for this lab 2. Using the resistor dial, select the resistor needed for the experiment 3. Using the LabView software, open the BatteryResistanceEnergyBalance.vi 4. Run the program by clicking on the white arrow at the top left of the screen, and create a file name for your program 5. Turn on the circuit board (<i>the LED light should come on</i>) 6. Note any changes in battery voltage, resistor temperature, and battery temperature 7. To stop the program, click STOP to record the data, and THEN turn off the board to decrease discrepancies in the data 	<p><i>The S1 switch operates the thermocouple connected to the 1Ω resistor. The S2 switch controls the low resistance bank and the S3 switch operates the high resistance bank.</i></p> <p><i>Since the resistors are in series, they are added up across the board, but remember to include the 1Ω resistor attached to the thermocouple. The far left wire connected to the dial is the short circuit, resulting in 0 Ohms.</i></p>
<p>III. Maintenance</p> <ol style="list-style-type: none"> a. The Module should be cooled for a minimum of 30 minutes before performing the next experiment since temperature measurements are very sensitive b. Be sure to disassemble the data acquisition cable, circuit board, and base holder and put away the materials when you leave 	

3.2.2. Governing Differential Equations

The students are responsible for the derivation of governing differential equations such as the equation for change in resistor temperature as a function of time, $\frac{dT_{res}}{dt}$ which can be derived from the change in internal energy over time; $\frac{dU}{dt}$. [27] The students are to identify how voltage drop and amperage translate to a heat input term in a first law balance, and they are to estimate parameters such as heat capacity and mass. They are encouraged to use MatLab to solve the differential equations that govern the system.

The following are pertinent governing equations:

$$\frac{dU}{dt} = Q - W \quad (3-1)$$

$$\frac{m_{res}C_{res}dT_{res}}{dt} = Q - W \quad (3-2)$$

$$\frac{m_{res}C_{res}dT_{res}}{dt} = V^2/R - hA(T_{res} - T_{ambient}) \quad (3-3)$$

3.2.3. Modeling Data

During initial predictions the students will typically neglect the convective cooling of the resistor by ambient air or they will struggle to identify how to model the heat transfer. Most students have not had a course in heat transfer, and when they identify the need to apply an engineering science that they have not yet covered they are directed to research the use of heat transfer coefficients. [28] The need to take into account the convective heat transfer term to model the temperature profile of the resistor will become evident when they obtain experimental temperature profiles. If convection was not identified during the predictive modeling stage of the project, the temperature profile indicates the need to modify the model battery. Figure 3-1 shows the raw experimental

data, and Figure 3-2 depicts the superimposed model after is is fitted with the experiental data. The modeling process provides a conceptual learning element because the students can visually relate how changing the heat transfer coefficients modifies the temperature profile.[22]

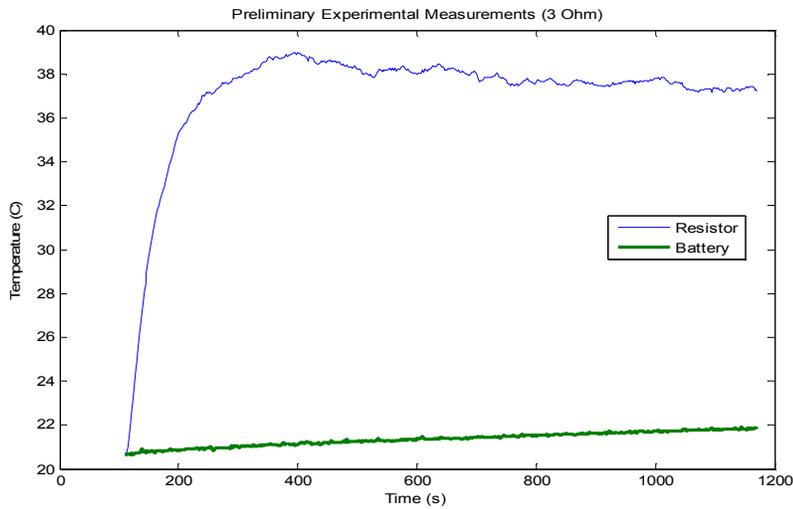


Figure 3-1 A plot of the resistor and battery temperature profile with a 3 Ohm total resistor.

Some of the modeling parameters are shown in Table 3-1 including heat transfer coefficients, heat capacity, total resistance applied to the battery, time span required to run the experiment, and initial temperature. These parameters are inputted into various MATLAB codes to model and plot the data.

Table 3-1 Sample parameters used model the resistor temperature versus time.

Model Parameters used for the Resistor Temperature vs. Time	
mC	1.675
hA	.255
R	3
T _{span}	[1, 289]
T _o	20.95

Figure 3-2 provides a typical resistor temperature versus time profile with modeling results and a voltage profile for battery discharge operating with a 3-ohm total resistance load.

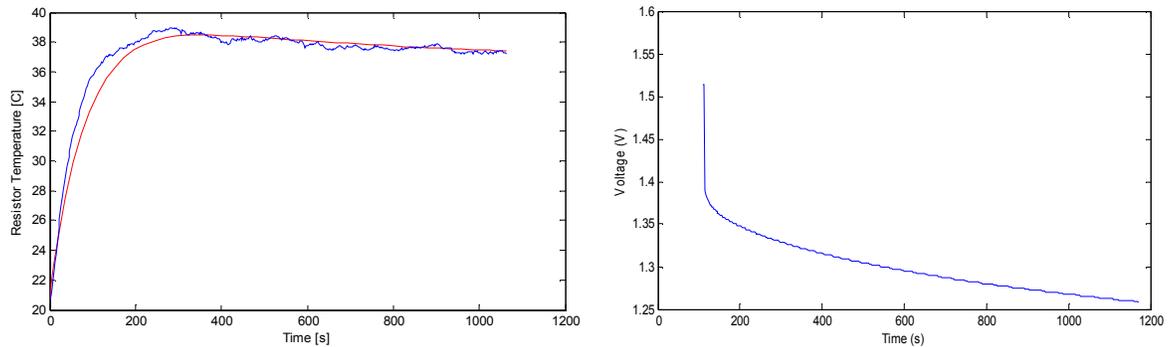


Figure 3-2 A plot of the resistor temperature with superimposition of modeling results (left) and voltage profile of the battery operating with a 3 Ohm total resistor (right).

The resistor temperature versus time profile can be used to model the resistor temperature as a function of time by manipulating hA , the heat transfer coefficient, and mC , the heat capacity, in the MATLAB program. The decreasing temperature is a manifestation of decreasing voltage power output from the AA battery which is under a heavy load.^[29] This aspect of the project introduces the challenge of how to handle the modeling of the resistor temperature for a non-constant voltage term—this introduces the utility for numerical solution of ordinary differential equations when analytical solutions may not be an option.^[30]

The voltage data shown in Figure 3-2 behaved accordingly to theory because there is a rapid decrease at first because a battery can only perform at its ideal for a short amount of time. The steep drop in voltage at the beginning of the plot is due to the power supply being turned on at the start of the experiment after the run has already begun. The voltage then gradually decreases as a slower rate as the time increases.

Another aspect of this lab can be used to measure battery efficiency by measuring actual voltage, shown in Figure 3-2, delivered by the battery divided by the ideal voltage. The students will be able to follow the temperature profile of the battery and visually understand and verify what happens to the lost energy.[31]

3.2.4. Other Applications

For semester-long projects, the students are able to sequentially perform the following:

1. Convert the voltage profile of Figure 3-2 to battery efficiency versus time.
2. Obtain battery voltages at a specified times (e.g. 30 seconds into discharge) over multiple resistances then use these data to prepare a battery performance curve (Voltage versus Amperage).
3. Fully deplete a battery to obtain the amp-hours of energy the battery is able to deliver and compare this to the mass of the battery components (as estimated based on Material Safety Data Sheet (MSDS) information).
4. Use the performance curve (from 2), amount of active reagent utilization (from 3), membrane surface area (membrane that separate cathode from anode, an estimated value) to design a battery for a different application (e.g. powering a 20 W light bulb for 2 hours).

A project based on these steps provides a valuable experiential leaning process involving: energy balances, transient energy balances, basic circuit theory, modeling versus predictive simulation, convective heat transfer, analytical versus numerical solution methods, mass balances, transient mass balances, battery performance curves, and product design.[32]

3.2.5. Sample Outline for Project 1: Battery Resistor Energy Balance

Project Objective

The purpose of this lab is to develop applications to measure and record temperature, voltage, current, and concentration of mass as a function of time. Virtual instruments will be used to simulate different systems by the use of various resistors and experimental data will be modeled as a function of time to describe how the battery and resistor work in a circuit.

Part A

Given project-specific settings for S1 and S2 (this is given), estimate the temperature of the 1 Ohm resistor when the circuit is closed based on initial conditions at ambient temperature. Perform a-e in this analysis. How long will it take for a temperature rise of 4°C?

- a. Derivation of governing differential equations.
 - Derive the equation for change in resistor temperature as a function of time, $\frac{dT_{res}}{dt}$ and include this in your report
- b. Simulation of system using analytical approaches a possible and using Matlab (including temperature increase). Each person will be given a specific resistance at which to model the resistor and the battery.
 - Use Matlab to define and solve the differential equation, and to import and plot the data
- c. Primary experimental measurements on the system.
 - Use project specific settings for S1 and S2

- Plot Battery and Resistor temperature together, and Voltage profile separately
- d. Modeling of experimental data
 - Model the temperature of the resistor as a function of time
 - Use Matlab m-files provided to fit your data by manipulating mC and hA

Part B

Battery efficiency can be obtained by measuring actual voltage delivered by the battery divided by the ideal voltage. What happens to the lost energy? Can you verify that this is happening? (NOTE: Here the students will need to follow the temperature profile of the battery.

- e. Comparing the two different resistances used in the experiment, which resistance caused the greater voltage drop and why?

Part C (Optional)

Based on the mass of the different components in the battery, estimate the Watt-hours of electrical power in the battery. Devise an experiment to completely discharge the battery in 30 minutes. Perform this experiment and compare results to your estimate.

- f. Extrapolation of model to allow specification of the battery to power the 10 W light bulb for 1 hour.

The following is a schematic of the experimental system shown in Figure 3-2. An AA battery is used to heat a 1 Ohm resistor. The temperature and voltage of both the battery and the resistor are monitored. Switches S1 and S2 can be varied to change the total

resistance of the circuit to allow additional data to be obtained and/or to allow different groups to have different project definitions while using the same experimental system.

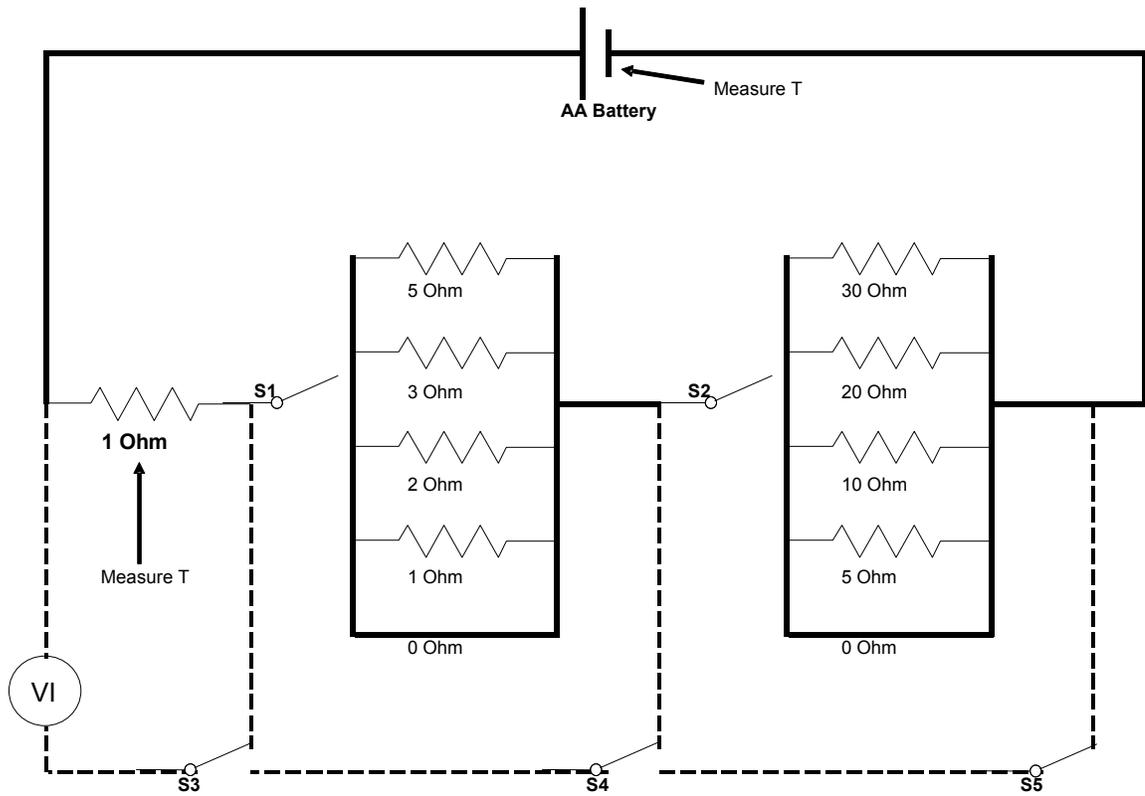


Figure 3-3 Schematic of resistor bank on module.

3.2.6. MatLAB Codes for Project 1: Battery Resistor Energy Balance

Data Import

```
uiimport
Time=data(:,1);
ResistorTemp=data(:,2);
BatteryTemp=data(:,3);
Voltage=data(:,4);
plot(Time, ResistorTemp)
hold all
plot(Time, BatteryTemp)
hold off
plot(Time, Voltage)
```

MEB Data Extraction

```
Time = data(:,1);      %Takes all values in first column of "data" array and gives it the
name "Time"
ResistorTemp = data(:,2); %Takes all values in second column of "data" array and gives
it the name "ResistorTemp"
BatteryTemp = data(:,3); % Takes all values in third column of "data" array and gives it
the name "BatteryTemp"
Voltage = data(:,4);   % Takes all values in forth column of "data" array and gives it
the name "Voltage"
InitialTime = Time(1,1) %Gives the initial time value
FinalTime = Time (289,1) %Gives the last time value...by looking at the "workspace"
tab my "data" array has a value of <1676x4 double> this means the array has 1676 lines
and 4 columns, so my "Time" array will have 1676 values and #1676 will be my final
time
InitialTemp = ResistorTemp(1,1) ) %Gives initial temperature to use as initial condition
in the differential equation
```

Dual Plot Solver

```
solver      %Use the name of ODE solver m-file you created previously
hold on     %Allows for multiple plots to be displayed on same figure
plot(Time- InitialTime,ResistorTemp)%Plots ResistorTemp as a function of Time
hold off    %Stops allowing plots to be added to same figure

                                %Adds axis titles and a legend to the figure
xlabel('Time [s]');
ylabel('Resistor Temperature [C]');
legend('Model','Experimental Data','Location','South');
```

Solver

```
tspan=[InitialTime FinalTime];  
T0=InitialTemp;  
[t,T] = ode45(@difftemp, tspan, T0);  
plot(t-InitialTime,T,'Color','red');
```

To Model Data

```
function Tprime = difftemp(t,T,mC,hA,P,R,Tamb);  
mC=1.675;  
hA=0.255;  
P=0.05291*exp(-0.0009862*t)+0.1703*exp(-2.636e-5*t);  
R=3;  
Tamb=20.95;  
Tprime = ((1/mC)*P)-((hA/mC)*T)+((hA/mC)*Tamb);
```


<p>V. Operational Procedures</p> <ol style="list-style-type: none"> 8. The switch configurations should be S1 down, S2 down, and S3 up for this lab 9. Using the resistor dial, select the resistor needed for the experiment 10. Using the LabView software, open the BatteryResistanceEnergyBalance.vi 11. Run the program by clicking on the white arrow at the top left of the screen, and create a file name for your program 12. Turn on the circuit board (<i>the LED light should come on</i>) 13. Note any changes in battery voltage, resistor temperature, and battery temperature 14. To stop the program, click STOP to record the data, and THEN turn off the board to decrease discrepancies in the data 	<p><i>The S1 switch operates the thermocouple connected to the 1Ω resistor. The S2 switch controls the low resistance bank and the S3 switch operates the high resistance bank.</i></p> <p><i>Since the resistors are in series, they are added up across the board, but remember to include the 1Ω resistor attached to the thermocouple. The far left wire connected to the dial is the short circuit, resulting in 0 Ohms.</i></p>
--	---

Analysis of the data for this project can be obtained by linear regression of an equation derived as follows.[33] Where:

$$V_o = I (R_{\text{Battery}} + R_{\text{Circuit}}) \quad (3-4)$$

The current (I) for each experiment can be identified by this same equation evaluated over the circuit load rather than the theoretical voltage of the battery:

$$I = V_{\text{Circuit}} / R_{\text{Circuit}} \quad (3-5)$$

Or

$$V_{\text{Circuit}} = V_o - R_{\text{Battery}}(V_{\text{Circuit}} / R_{\text{Circuit}}) \quad (3-6)$$

Where linear regression can be used to identify V_o (constant) and R_{Battery} (slope).

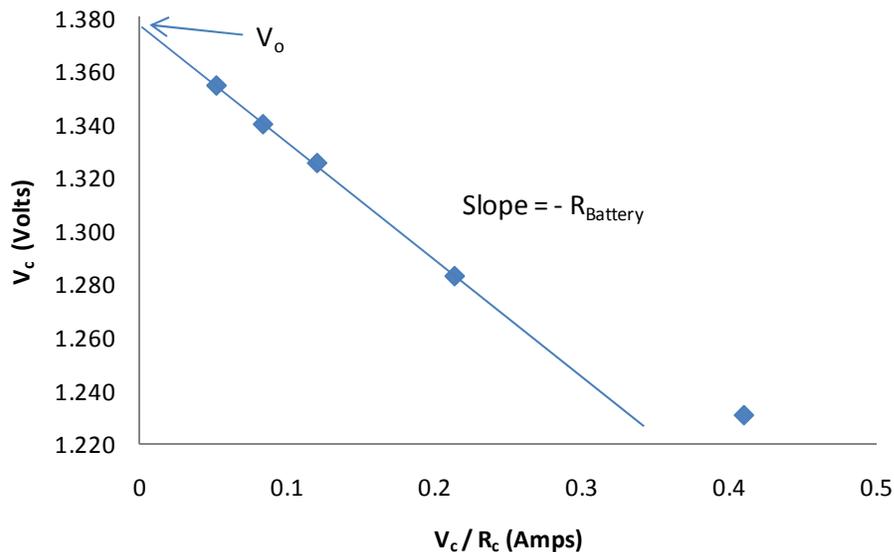


Figure 3-5 Example results from PROJECT 2 and equation 3-6 for evaluating the internal resistance of a battery. The data are for different circuit resistances evaluated with the experimental module.

Figure 3-5 illustrates experimental data plotted according to equation 3-6 with an excellent correlation and little scatter. The students are expected to analyze their data and understand why the internal resistance of the battery stays constant, using equations to justify their results. The internal resistance of the battery is relatively constant for data taken at a constant time of exposure to a load. For low resistances, the resistance of the battery will decrease with time due to increased diffusion over-potential as the substrates closest to the membrane are consumed.[34] This trend is seen for the right-most data point, and for this reason, the linear regression was performed without including that data point.

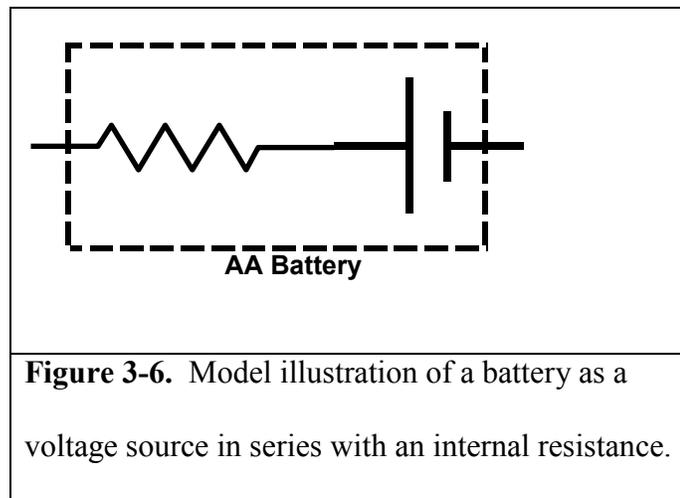
Extensions of this project could include evaluating the internal battery resistance at different times the battery is under load.[35] Detailed discussions related to transient diffusions in packed-bed anodes could be used to explain the dependence of the internal battery resistance on time. If the students are able to do the sophisticated modeling, the

diffusion in the packed bed could be modeled, converted to diffusion over-potential, and interpreted in terms of a resistor model.

3.2. Sample Outline for Project 2

Project Outline: Evaluating the Internal Resistance of a Battery

Phase 1 – A common representation of a battery for circuit representation purposes is as a resistor in series with a voltage source (see Figure 3-6). In the first phase of this experiment, you are to evaluate an AA battery for about 10 seconds at each of several module-set resistances (from high to low) to evaluate if this model of a battery is accurate. The experimental component of this phase should take about 5 minutes.



- a. Run the module for 10 seconds, and note the open- circuit voltage and the voltage at the 10 second interval. **Use this information to find the internal resistance of the battery (R_B) of each resistance and compare them to each other.**
 - i. Open a new file each run, and use the following total resistances to run your module: **3Ω , 6Ω , 11Ω , 16Ω , 26Ω , 36Ω**

3.4 Project 3: Diffusion and Permeability in a Manganese Dioxide-Zinc Battery

The objective of this project is to evaluate batteries that the students assemble. The students are also to relate fundamental differences of the battery performances to properties of the materials and the cell geometry, and to quantitatively correlate the performance to diffusivity resulting from varying the separator material. The use of a zinc electrode anode is important because of its high open-circuit voltage in the KOH electrolyte, a low corrosion rate, and a low material cost.[36]

A schematic of the battery assembly is provided by Figure 3-7. Prepared anode packing, cathode packing, separator materials, and premixed electrolyte are provided to the students for assembling the batteries. The electrode packings are volumetrically dispensed into the cell being separated by the separator materials. Alligator clips are used to connect the current collectors of the battery assembly to the AA battery holder points of contact on the experimental module.

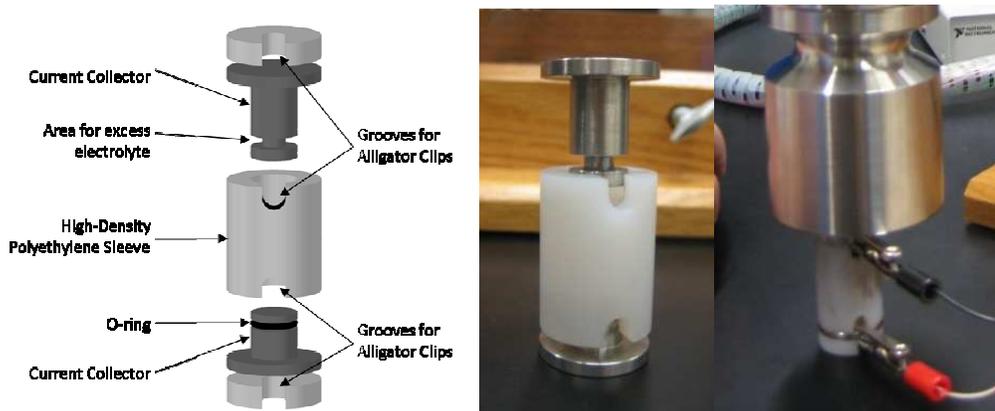
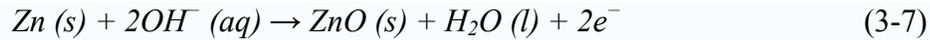


Figure 3-7 Pictorial representation of a compression cell used for the assembly of MnO_2 – Zn batteries (left) with picture of assembled cell (middle) and an assembled cell with weight to provide compression (right).

The experimental procedures include assembling several Zn- MnO_2 batteries with different separator materials and evaluate the performance in a 33-ohm circuit. Zinc powder is used as the anode packing in preference to zinc foil or plates because of its

large surface area to distribute solid and liquid phases more homogeneously.[37] A high zinc surface area to volume ratio is needed for high-rate capability and zinc oxide will form on the surface of the zinc as summarized by the following half reactions:[38]



Manganese oxide powder mixed with a carbon black is used as the cathode. The carbon is used to increase conductivity of the positive active mass to reduce the internal resistance of the cell.[39] This material may require mechanical processing to maximize reactivity.[40] Potassium hydroxide (1M or 2M) in distilled water works well as the electrolyte because of its high conductivity, and results in a low internal resistance.[41] In the presence of KOH, the discharge behavior of MnO₂ occurs in a heterogeneous phase reaction.[42]

3.4.1. Laboratory Operational Procedures

Phase II: Battery Assembly of Zn- MnO ₂	
Procedure	Principle
<p>***EYE PROTECTION AND GLOVES REQUIRED***</p> <p>VI. Operating Procedures</p> <ol style="list-style-type: none"> Obtain a Compression Cell and a 6Kg weight In the glove box, start to assemble the battery by inserting the base of the compression cell first (the shorter piston) Place ~0.15g of the cathode material (MnO₂) into the cylinder (enough to cover a thin layer on the bottom of the cell) and tap the cell to create an even distribution 	<p><i>Keep in mind which side of the compression cell the anode or cathode material is being placed. This is important when connecting the positive and negative leads</i></p> <p><i>Use the spatula to flatten out the filter paper and tap out the excess cathode material</i></p>

<p>d. Cover the material with the correct number of filter papers</p> <p>e. Wet the filter paper by placing a few drops of the electrolyte solution (~10-15 drops of 1M KOH)</p> <p>f. Add ~ 0.5g of the anode material (Zn) and close the compression cell with the longer piston</p> <p>g. Bring the assembled battery back to the module and obtain a pair of wires. Remove the original AA battery and snap off the black wire snaps and connect them to your wires.</p> <p>h. Attach the alligator clips to your assembled battery. Then put the 2 plastic pieces on either side of the battery, aligning them with the notches.</p> <p>i. Place 6Kg of weight on your battery and run the program (a good open circuit reading should be ~1.4V)</p>	<p><i>Potassium Hydroxide is used as an electrolyte in Manganese Dioxide-Zinc batteries because of its strong conductivity</i></p> <p><i>There should be about the same amount of Zn to MnO₂, however the Zn is a heavier metal, so it has a higher weight</i></p> <p><i>The BLACK lead attaches to the ANODE and the RED lead attaches to the CATHODE. Pay attention to the colors on the clips, NOT necessarily on the wires.</i></p> <p><i>The weight on the battery compresses the anode and cathode material together, making the electrons flow more efficiently, and creating a better voltage</i></p>
<p>I. Maintenance</p> <p>a. Be sure to disassemble the data acquisition cable, circuit board, and base holder and put away the materials when you leave</p> <p>b. Also, clean the compression cell so that it is ready for the next group</p>	

3.4.2. Separator Material for Cathode and Anode

The separator materials provide the best opportunity to systematically vary a parameter that impacts battery performance. Sheets of permeable material can be punched to sizes that match the inner diameter of the battery's polyethylene sleeve. When preparing the battery, care must be taken to assure that the permeable separator totally separates the anode from the cathode or the battery will short circuit. Filter paper work well as separators with the experimental parameter being the number of sheets of filter paper placed between the anode and cathode. The filter paper used in this experiment is a qualitative type with course porosity and a fast flow rate from Fisher Brand. More sheets will create greater resistance to diffusion and greater over-potential losses.[34] It is also beneficial to have a negative control of a non-permeable polypropylene membrane to confirm that in the absence of a diffusive path between the anode and cathode, the battery voltage will immediately go to zero.

The test cell (Figure 3-7) is basically a compression cell comprised of two pistons inside a non-conductive sleeve. The battery is assembled by inserting the base of the compression cell first (the shorter piston). It is assembled as follows:

1. Place a volumetrically dispersed amount of the cathode material (MnO_2) into the cylinder (enough to cover a thin layer on the bottom of the cell) and tap the cell to create an even distribution.
2. Cover the material with the correct number of filter papers (qualitative P8 Fisher Brand).

3. Wet the filter paper by placing a few drops of the electrolyte solution (~10-15 drops of 1M KOH). *Potassium Hydroxide is used as an electrolyte in Manganese Dioxide-Zinc batteries because of its strong conductivity.*
4. Add a thin layer of the anode material (Zn) and close the compression cell with the longer piston.
5. Bring the assembled battery back to the module and obtain a pair of wires. Remove the original AA battery, snap off the battery power adapters and connect them to the wires.
6. Attach the alligator clips to the assembled battery and put the two plastic pieces on the top and bottom of the assembled battery, aligning them with the notches.
7. Place a 6 kg weight on the assembled battery and run the program. The weight on the battery compresses the anode and cathode material together, making the electrons flow more efficiently, and creates a better voltage.[43]

3.4.3. Diffusivity and Permeability Results

Figure 3-8 summarizes representative data for a study of 2, 4, and 6 layers of filter paper, and a negative control using polypropylene as a non-permeable membrane separating the anode material from the cathode material keeping the time of the experimental runs constant. The polypropylene membranes used in this experiment were obtained using the same hole-punch technique as the filter papers, using a petri-dish as the material. Battery performance typically consists of a steep drop in voltage initially and then a steady decline. At a constant load, an increase in resistance (more layers of filter paper) results in a lower voltage delivered to the resistor.[34] Ideally, the voltage for the non-permeable membrane should immediately drop to zero, however, because of

the difficulties involved in constructing a perfect separation seal, there may be some voltage detected due to the seepage and mixing of the anodic and cathodic material around the outer perimeter of the polypropylene membrane.

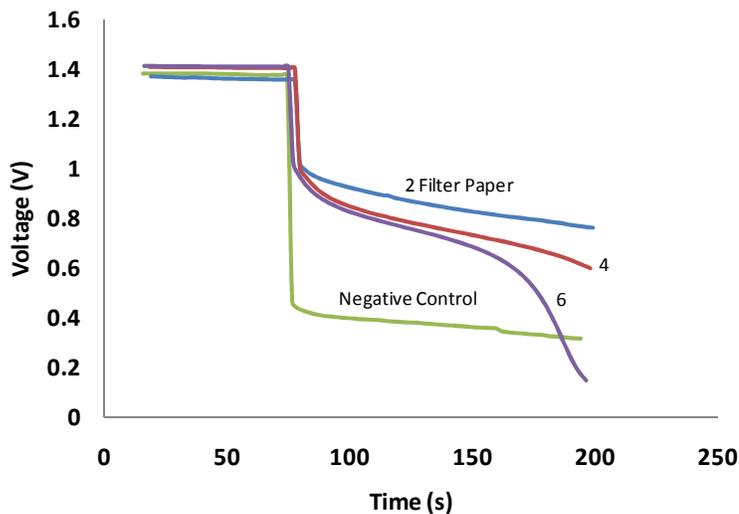


Figure 3-8 Graph of results showing proposed trend of decreasing voltage with increasing resistance of separator between electrodes. The numbers indicate the number of layers of filter paper between the electrodes.

The students should be able to qualitatively understand how increased diffusion distances through permeable materials translate to increased voltage over-potentials.[34] In more advanced applications, the permeability can be related to voltage. Other variations from this experiment include use of battery assemblies with different inner diameters and use of non-permeable separators cut into washer-shapes that vary the cross-sectional area available for diffusion.

3.4.4. Sample Outline for Project 3

Project Outline: Diffusivity and Permeability in a Manganese Dioxide- Zinc Battery

Phase 2 –You are to assemble several Zn-MnO₂ batteries with different materials (specified in group project specification) separating the anode from the cathode. The

assembled battery will be connected to the module via wire leads. We will run the total resistance of the battery at 33 Ohms. Use Figure 3-9 as a schematic for the resistor bank for reference.

- a. Each group will assemble their battery with a negative control, 2, 4, and 6 filter papers separating the anode material from the cathode material to witness the ion's diffusivity and to notice a trend regarding voltage, current, and the layers of filters with respect to time.
 - a. The negative control will be used with a polypropylene non-permeable membrane.
- b. Run the LabVIEW program using the assembled battery; you will notice a steep drop in voltage initially and then a steady decline. *A good Zinc battery should have about 1.4V at open circuit.* Stop the program at 2 minutes. And then, turn the module OFF.
- c. Using MatLAB, import the files and define your variables using this code in the command prompt:

```
uiimport
Time=data(:,1);
ResistorTemp=data(:,2);
BatteryTemp=data(:,3);
Voltage= data(:,4);
plot(Time, Voltage)
I= Voltage./(Total Resistance)
```

- i. When you import your data, cut out the voltage data in open circuit using the header function
- ii. The Total Resistance should be the resistance that was assigned earlier. This gives an equation for Current.

- iii. The use the function trapz(Time, I) in the command line to integrate the current to obtain Coulombs. Then divide by Faraday's constant to obtain moles of electrons.
- d. Plot all 4 experimental runs on the same graph with respect to time. Make 2 separate graphs: Voltage vs. Time, and Current vs. Time
- e. Evaluate the diffusivity of the battery if there is a consistent trend. Relate the flow of ions through the electrolyte solution to the thickness of the filters separating the cathode and anode material. Use the mass flux equation and Fick's law of diffusivity to support your answer.
- f. Calculate the total power output of each experimental run by integrating Power/Time and discuss your results.

Objective - The objective is to relate fundamental differences of the battery performances to thermodynamic properties of the materials and the cell geometry, and to quantitatively relate the performance to diffusivity (or apparent diffusivity/permeability) of your separator material.

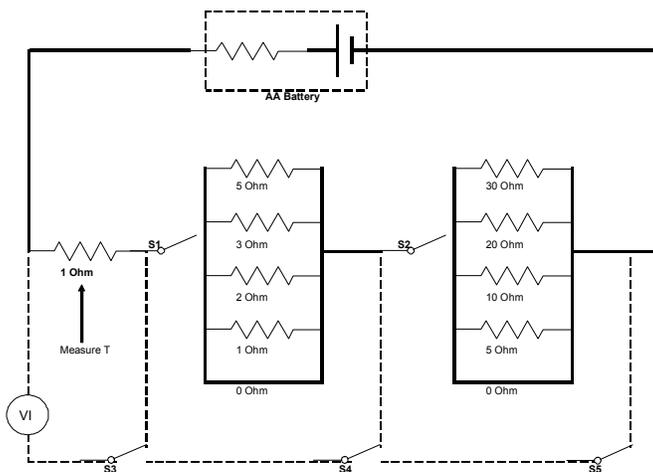


Figure 3-9 Schematic of resistor bank.

3.5 Student Feedback

For Project 1, the students recognized and appreciated how energy is converted from chemical to thermal forms and how transient differential models can relate underlying engineering science (ohms law, convective heat transfer) to observed phenomena. The most frequent problem encountered was a lack of attention by the students on which voltages were actually being measured during the experiment. Project 2 was a simple and straight forward experiment that validates a commonly used model for batteries. Students that expected the need for a detailed analysis based on differential equations were disappointed. Project 3 was effective in getting students to contemplate some more complicated aspects of mass transfer and how mass transfer limits the performance of a battery. The primary concern with Project 3 was that sloppy preparation of the assembled battery could result in inconsistent data.

3.6 Conclusion

The battery provides an excellent basis for student projects in chemical engineering. The module described in this paper provides a way to delivery experiential learning with batteries in open formats that can be used with a variety of lecture-based courses. The students are able to directly connect with what they observe in the experiential learning because they encounter and frequently use batteries in their day-to-day routines. Different variations of battery-based projects allow students to use energy balances, transient energy balances, basic circuit theory, modeling versus predictive simulation, convective heat transfer, analytical versus numerical solution methods, mass balances, transient mass balances, battery performance curves, and product design.

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