UK Research Needs in Grid Scale Energy Storage Technologies

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Preface

This white paper provides a concise guide to key technology options for grid scale energy storage, with the aim of informing stakeholders in industry, government and the funding agencies of the opportunities and need for underpinning research into both current and emerging technologies for grid scale storage applications.

The paper has been produced in recognition of both the need for cost effective, durable and safe grid scale energy storage solutions (across a wide range of power and energy levels) to support future low carbon energy systems and the need for underpinning research into new ideas and concepts to support the development and subsequent deployment of both emerging and new energy storage options.

The paper is based on the personal views of contributors from a number of EPSRC funded programmes: "Energy Storage for Low Carbon Grids" (EP/K002252/1), "Integrated, Market-fit and Affordable Grid-scale Energy Storage (IMAGES)" (EP/K002228/1), the Energy SuperStore SUPERGEN Hub (EP/L019469/1) and the Energy Storage Research Network (EP/J021695/1).

The Energy SUPERSTORE is the UK's Energy Storage Supergen Hub. This Hub aims to accelerate innovation by developing the UK Energy Storage community, bringing together researchers from the academic, industrial and policy domains. The Hub is supported by the EPSRC through grant EP/L019469/1.

The Energy Storage Research Network (ESRN) is the networking and events arm of the Energy SUPERSTORE, promoting collaboration in energy storage and its application to future low carbon energy systems. This network is supported by funding from the EPSRC through grant EP/J021695/1.

The EPSRC leads the Research Councils UK (RCUK) Energy Programme, which aims to position the UK to meet its energy and environmental targets and policy goals through world-class research and training. The Energy Programme is investing more than £625 million in research and skills to pioneer a low carbon future. This builds on an investment of £839 million over the past eight years.

Executive summary

In response to the climate change challenge, the UK's electricity system is expected to integrate significant amounts of intermittent renewable generation, potentially in combination with less flexible nuclear and CCS plants, while segments of the transport and heat sectors are expected to be increasingly electrified. Integration of low capacity value intermittent generation accompanied with possibly very significant increases in peak demand driven by transport and heating electrification, may lead to significant degradation in the utilisation of generation infrastructure and electricity network assets, leading to considerable increases in system integration costs.

In this context, grid scale energy storage can deliver multiple benefits to the system by: (i) reducing generation operating cost by enhancing the ability of the system to absorb renewable generation, reducing the curtailment of renewables; (ii) reducing generation investment costs by contributing to the delivery of adequacy / security of supply and (iii) offsetting the need for interconnection and transmission investment. Furthermore, smaller scale distributed storage can, in addition: (iv) reduce the need for distribution network reinforcement driven by the electrification of transport and heat sectors, while the most significant savings enabled by storage are in (v) reducing the need for investment in low carbon generation, while meeting carbon emission reduction targets.

This white paper provides a concise guide to key technology options for grid scale energy storage, with the aim of informing stakeholders in industry, government and the funding agencies of the opportunities and need for underpinning research into both current and emerging technologies for grid scale storage applications. The paper has been produced in recognition of both the need for cost effective, durable and safe grid scale energy storage solutions (across a wide range of power and energy levels) to support future low carbon energy systems and the need for underpinning research into new ideas and concepts to support the development and subsequent deployment of both emerging and new energy storage options.

It is evident that the UK, as an island nation with ambitious carbon reduction targets, will place increasing value on the flexibility offered by energy storage to manage its transition to a low carbon energy system. It is also clear that no single energy storage technology will meet the needs of the future energy system, with a range of services requiring a range of storage characteristics, from the rapid delivery of power in a matter of seconds, through to longer term energy storage over hours, days or weeks. It is also evident that the UK has significant research strengths across a number of the potentially critical energy storage technologies and their integration, along with innovative companies seeking to develop, demonstrate and commercialise energy storage solutions.

The paper does not attempt to cover all the possible ranges of storage technology options, but rather focuses on those where the UK has world class science and engineering research across its universities, as well as companies undertaking technology development, namely: lithium and sodium ion batteries; supercapacitors; aqueous batteries; flow batteries; compressed air energy storage; thermal energy storage; power to gas and the control and integration of energy storage.

The report sets out the views of the authors on the critical research needs facing this sector, if we are to deliver cost effective storage solutions in an appropriate timescale. The report does not seek to set out the market or regulatory barriers that face the sector today, though these are clearly also important barriers to success. What is clear is that we need to both learn by doing today, to scale up and re-risk promising technologies and to develop our strategies to interface and control storage technologies. In addition, we need to support the underpinning research that will continue to drive down cost and increase lifetime in the future, both by improving today's storage solutions and by developing new solutions based around alternate chemistries, materials and/or concepts, further discussion of which can be found within this report.

List of figures and tables

List of abbreviations

\$ / kWh	Dollars per kilowatt-hour
\$ / ton	Dollars per tonne
°C	Degrees Celsius: unit of temperature.
$\mu F / cm^2$	Microfarads per square centimetre: unit of capacitance.
µm	Micrometre: one millionth of a metre.
3D	Three dimensional
AC	Alternating Current
A-CAES	Adiabatic Compressed Air Energy Storage
atm	Atmospheres: unit of pressure.
C	Capacitance, measured in farads per square metre.
ca.	Circa / approximately
c.f.	Compared with (from the Latin, conferre).
CAES	Compressed Air Energy Storage
CCS	Carbon Capture and Storage
CES	Cryogenic Energy Storage
CH_4	Methane
CO_2	Carbon dioxide
CSP	Concentrated Solar Power
CuO	Copper oxide
CuZn	Copper Zinc
d	Thickness, measured in millimetres.
DC	Direct Current
DOD	Depth Of Discharge
E	Energy in a charged capacitor, measured in Joules (J).

EDL	Electric Double Layer
EES	Electrical Energy Storage
Energy SUPERSTORE	The UK Energy Storage SUPERGEN Hub
EPSRC	Engineering and Physical Sciences Research Council
ES	Executive Summary
ES4LCG	Energy Storage for Low Carbon Grids Grand Challenge project
ESRN	Energy Storage Research Network
ETI	Energy Technologies Institute
EUR	Estimated Ultimate Recovery
EV	Electric Vehicle
F / g	Farads per gram: unit of capacitance.
$Fe(III)PO_4$	Iron phosphate
Fe/Cr	Iron Chromium (ICB): a type of flow battery.
FeS	Iron (II) sulphide
g	Gram
g / mol	Grams per mole
g CO^2 / kWh	Grams of carbon dioxide per kilowatt hour
GVEA	Golden Valley Electric Association
GW	Gigawatt
GWh	Gigawatt hour
HES	Heat Energy Storage
HVDC	High Voltage Direct Current
Hz	Hertz: unit of frequency.
IGBT	Insulated Gate Bipolar Transistor
IMAGES	Integrated, Market-fit and Affordable Grid-scale Energy Storage
IPCC	Intergovernmental Panel on Climate Change

ISO	International Organisation for Standardisation
J	Joule: unit of energy.
kg	Kilogram
kJ	Kilojoule: unit of energy equivalent to a thousand joules.
km	Kilometre
KOH	Potassium hydroxide: an electrolyte used in electrolysers.
kW	Kilowatt: unit of power equivalent to 1 kilojoule (kJ) of energy expended per second.
kWe	Kilowatt electric: the electric output of a power plant in kilowatts.
kWh	Kilowatt hour: unit of energy equivalent to one kilowatt (1 kW) of power expended for one hour of time.
LAES	Liquid Air Energy Storage
LFP	$LiFePO_4$, lithium iron phosphate.
LHS	Liquid Heat Storage
Li	Lithium
Li_2CO_3	Lithium carbonate
Li_2FeSiO_4	A lithium metal orthosilicate typically used as the material for cathodes in a lithium ion battery.
$Li_4Ti_5O_{12}$	Lithium Titanate
$LiBF_4$	Lithium tetrafluoroborate: a salt typically used as the electrolyte in a lithium ion battery.
LiC_6	Lithium graphite
$LiFe(II)PO_4$	Lithium iron phosphate, typically used to make Li-ion cathodes.
Li-ion	Lithium ion (battery)
$LiMn_2O_4$	A cubic spinel used for the positive electrode in "rocking-chair" batteries.
$LiN(CF_2SO_3)_2$	A lithium sulfonate salt, typically used as the electrolyte in a lithium ion battery.
$LiNi_xMn_yCo_zO_2$ $(x+y+z=1)$	NMC: Nickel manganese cobalt, a material used for grid-scale lithium-ion battery cathodes.

$LiNO_3$	Lithium nitrate
$LiPF_6$	Lithium hexafluorophosphate, a salt typically used as the electrolyte in a lithium ion battery.
LNCA or LNCAO	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, used as a cathode in some Li-ion batteries.
LTO	Lithium titanate
m	Metre
M	Molar
m^2 / g	Square metres per gram: unit of specific surface area.
m^3	Cubic metre: unit of volume.
mAh	Milli-ampere hours, commonly used to describe the energy charge that a battery will hold and how long a device will run before the battery needs recharging.
mAh / g	Milli-ampere hours per gram.
min	Minute
MJ	Megajoule: unit of energy equivalent to a million joules.
MJ / m^3	Megajoules per cubic metre
mm	Millimetre: 1/1000th of a metre.
MML	Modular Multi-Level
MnO_x	Manganese oxides
mol / L	Moles per litre
ms	Milliseconds: 1/1000th of a second.
MVA	Megavolt amperes
MW	Megawatt: unit of power equivalent to 1 megajoule (MJ) of energy expended per second.
MWe	Megawatt electric: the electric output of a power plant in megawatts.
MWh	Megawatt hour: unit of energy equivalent to one megawatt (1 MW) of power expended for one hour of time.
N_2	Nitrogen

Na	Sodium
$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$	Sodium [iron/manganese] oxide
Na_2CO_3	Sodium carbonate
$Na_2Fe_2(SO_4)_3$	Sodium-based alluaudite-type sulphate framework.
$Na_2FeP_2O_7$	Sodium pyrophosphate
Na_2SO_3	Sodium sulphite
Na_2SO_4	Sodium sulphate
Na-ion	Sodium ion (battery)
$NaMnO_2$	Sodium manganese oxide, the material used for the cathode in an Aqueous Hybrid Ion battery.
$NaPF_6$	Sodium hexafluorophosphate, a salt used as a non-aqueous electrolyte in Na-ion batteries.
NaS	Sodium sulphur
$NaTi_2(PO_4)_3$	Sodium titanium phosphate
NEC	Nippon Electric Company
NGO	Non-Governmental Organisation
NiCd	Nickel cadmium
NiFe	Nickel iron
NiMH	Nickel Metal Hydride
NiO.OH	Nickel oxy-hydroxide
NMC	$LiNi_xMn_yCo_zO_2$ ($x+y+z=1$): Nickel manganese cobalt, a material used for grid-scale lithium-ion battery cathodes.
OCP	Open-Circuit Potential
P	Power density
P2G	Power to Gas
pa	Per annum
PbO_2	Lead oxide, used for the positive electrode in lead acid batteries.
$PbSO_4$	Lead sulphate: nearly insoluble crystals which precipitate during the

	discharging process in lead acid batteries.
PEM	Polymer Electrolyte Membrane
pH	A measure of how acidic/basic a solution is.
PHS	Pumped Hydro Storage
PNNL	Pacific Northwest National Laboratory
ppm	Parts per million
PTES	Pumped Thermal Electricity Storage
PV	Photovoltaic
R	Resistance, measured in ohms.
RCUK	UK Research Council
RFB	Redox Flow Battery
RuO_2	Ruthenium oxide
s	seconds
S / cm	Siemens per centimetre: unit of electrical conductivity.
SA	Surface Area
SEI	Solid Electrolyte Interphase
SHS	Sensible heat storage
Si	Silicon
SO_2	Sulphur dioxide
SOC	State-Of-Charge
SSE	Scottish and Southern Energy: SSE plc is a British energy company operating in Ireland and the UK.
TCES	ThermoChemical Energy Storage
TES	Thermal Energy Storage
TiO_x	Titanium oxides, considered for battery anode materials.
UPS	Uninterrupted Power Supply
US DoE	US Department of Energy

V	Voltage
V2G	vehicle-to-grid
VO_2	Vanadium (IV) oxide, used for the negative electrode in the first aqueous Li-ion battery.
vol	Volume
VO_x	Vanadium oxides, considered for battery anode materials.
VRFB	All-Vanadium Redox Flow Battery
W	Watt: unit of power equivalent to 1 joule (J) of energy expended per second.
W / cm^2	Watts per square centimetre: unit of power density.
W / kg	Watts per kilogram, unit of specific power.
W / L	Watts per litre, unit of power density.
Wh	Watt-hour: unit of energy equivalent to one watt (1 W) of power expended for one hour of time.
Wh / kg	Watt hours per kilogram: unit of specific energy.
Wh / L	Watt hours per litre: unit of energy density.
Zn/Br	Zinc-bromine: a type of flow battery.
$ZnBr_2$	Zinc bromide, the electrolyte used in Zn/Br flow batteries.
ε_0	Vacuum permittivity (8.85×10^{-12} m^{-3} kg^{-1} s^4 A^2)
ε_r	Relative permittivity of a material, measured in farads per metre.
ρ	Density, or mass per unit volume.

Contents

1. Introduction

This white paper aims to provide a concise but authoritative guide to key technology options for grid scale energy storage, with a particular focus on informing stakeholders in industry, government and funding agencies of the opportunities and need for underpinning research into both current and emerging technologies for grid scale storage applications. The paper has been produced in recognition of both the need for cost effective, durable and safe grid scale energy storage solutions (across a wide range of power and energy levels) to support future low carbon energy systems and the need for underpinning research into new ideas and concepts to support the development and subsequent deployment of both emerging and new energy storage options.

The paper addresses the following energy storage options: lithium and sodium ion batteries; supercapacitors; aqueous batteries; flow batteries; compressed air energy storage; thermal energy storage; power to gas and the control and integration of energy storage. This paper does not attempt to cover all the possible ranges of storage technology options, but rather focuses on those where the UK has world class science and engineering research across its universities, as well as companies undertaking technology development.

The paper contributes to the road map for energy storage research being undertaken by the Energy SUPERSTORE and contains contributions from UK academics working within the two Grand Challenge projects in grid scale storage: Energy Storage for Low Carbon Grids (EP/K002252/1) and Integrated, Market-fit and Affordable Grid-scale Energy Storage (EP/K002228/1), all funded by the UK Research Council Energy programme.

2. The role of energy storage in low carbon grids

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In response to the climate change challenge, the UK's electricity system is expected to integrate significant amounts of intermittent renewable generation, potentially in combination with less flexible nuclear and Carbon Capture and Storage (CCS), while segments of the transport and heat sectors are expected to be increasingly electrified. Integration of the low capacity value intermittent generation, accompanied with possibly very significant increases in peak demand driven by transport and heating electrification, may lead to significant degradation in the utilisation of generation infrastructure and electricity network assets, leading to considerable increases in system integration costs.

> Energy storage delivers multiple benefits to the system.

Analysis at Imperial College London [1, 2, 3] has shown that, in the context of various potential low carbon electricity systems in the UK, energy storage delivers multiple benefits to the system. Grid scale storage technologies: (i) reduce generation operating cost by enhancing the ability of the system to absorb renewable generation, thereby reducing the curtailment of renewables; (ii) reduce generation investment costs by contributing to the delivery of adequacy / security of supply and (iii) offset the need for interconnection and transmission investment. Furthermore, smaller scale distributed storage can, in addition: (iv) reduce the need for distribution network reinforcement driven by electrification of the transport and heat sectors, while the most significant savings enabled by storage are in: (v) reducing the need for investment in low carbon generation, while meeting carbon emission reduction targets.

FIGURE 2.1
Optimal UK generation mixes with no flexibility (left) and with high flexibility (right), delivered through energy storage and demand side response, both achieving emissions of 50 gCO_2 / kWh.

Clearly, as the system is unable to accommodate the high penetration of low carbon generation required for compliance with the carbon emission targets, if storage is not available then significant additional capacity of low carbon generation would need to be built. As adding storage increases the ability of the system to integrate low carbon generation, fewer of the costly low carbon plants need to be built, leading to significant savings. Net system savings through the deployment of energy storage increase radically between 2020 and 2050, given the assumptions associated with the growth in intermittent renewable generation and levels of electrification. For example, the achievable net annual system benefits generated by storage range from £0.12 billion in 2020, to around £2-5 billion in 2030, while in 2050 they show a further rapid increase to over £10-15 billion per year.

> As adding storage increases the ability of the system to integrate low carbon generation, fewer of the costly low carbon plants need to be built, leading to significant savings.

Energy storage plays a major role in defining the optimal mix of low carbon generation technologies to deliver cost effective evolution to the UK low carbon energy system. With very low levels of deployment of energy storage in the system, the technologies to deliver a decarbonised electricity system would be primarily nuclear and, to a lesser extent, involve CCS. As shown in Figure 2.1, no wind or photovoltaic generation would be selected as part of the optimal generation portfolio, suggesting that the integration cost of renewable generation is comparatively higher than that of nuclear generation.

> Energy storage plays a major role in defining the optimal mix of low carbon generation technologies to deliver cost effective evolution to the UK low carbon energy system.

When a high level of flexibility is made available through demand side response and cost effective energy storage technologies, there is a significant shift towards renewable technologies in the generation mix. Figure 2.1 shows that more than 100 GW of combined wind and PV capacity can be accommodated, reflecting the reduced integration cost of renewable energy technologies enabled by the enhanced flexibility that energy storage can provide. Nuclear capacity is still present, although with a far lower volume (reduced from 33 to 9.9 GW), while the cost of CCS based electricity generation is not found to be competitive. This strongly demonstrates that energy storage technologies will be critical for designing cost-effective, decarbonised electricity systems in the future.

It is also clear that different types of energy storage will be needed to address this market, to deliver different services to the grid and to end-users. These range from energy storage technologies that deliver mostly energy, such as pumped hydro, compressed air, flow batteries, power to gas, liquid air, pumped heat, etc., to those that deliver mostly power, for example supercapacitors or flywheels and to those delivering some combination of both power and energy, such as batteries. It is therefore clear that there is no one single ‘winning’ energy storage technology, but rather that a portfolio of technologies needs to be developed to deliver cost effective, durable and safe energy storage solutions, supporting UK grid decarbonisation.

> There is no one single 'winning' energy storage technology.

In this context, accelerating the research and development of a range of grid scale electricity storage solutions promises substantial benefits in terms of energy cost and carbon footprint reduction, to a level that may set international standards. In this context, fundamental research in energy storage technologies is needed to address the challenge of decarbonisation posed by the global transition to renewables and other new low carbon energy sources. As an island, the UK is facing a very significant balancing challenge and will need solutions earlier than many other jurisdictions, hence the fundamental research conducted in the UK could turn this threat into an opportunity, providing leadership in the research and development of a range of energy storage technologies, many of which are discussed in this report.

> As an island, the UK is facing a very significant balancing challenge and will need solutions earlier than many other jurisdictions.

3. Lithium and sodium ion batteries

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Transforming lithium-ion (Li-ion) batteries so that they meet the needs of grid storage requires a step-change in the technology. Currently, the cost is too high, the calendar and cycle life too low and safety needs to be improved. Driven in part by the cost challenge, there is growing interest in the alternative sodium-ion (Na-ion) battery technology. Sodium is more abundant and hence cheaper than lithium. There is also considerable scope for the discovery of new electrodes and electrolytes that might outperform their lithium counterparts. The current research challenges involve the improvement of Li-ion batteries to deliver higher performance, low cost synthesis of electrode materials and the use of safer materials. The key challenge for Na-ion batteries lies in the development of new electrode and electrolyte materials.

> Sodium is more abundant and hence cheaper than lithium.

3.1. Introduction to the technology

Li-ion batteries consist of a cathode (positive electrode) and anode (negative electrode) with an electrolyte between, supporting the movement of lithium ions from one electrode to the other during charge and discharge. During charge, the lithium ions migrate from the cathode to the anode through the electrolyte while electrons flow through an external circuit in the same direction; during discharge, the reaction is reversed, supplying power.

The cathode usually consists of a metal oxide material, containing lithium, and the anode is usually graphite. Both materials allow the insertion and extraction of lithium ions. The electrolyte is typically composed of a salt (e.g. $LiPF_6$, $LiBF_4$ or $LiN(CF_2SO_3)_2$) dissolved in an organic solution (e.g. ethylene carbonate, dimethyl carbonate).

For example, in grid scale applications, Li-ion batteries are based on lithium iron phosphate cathodes and graphite anodes.

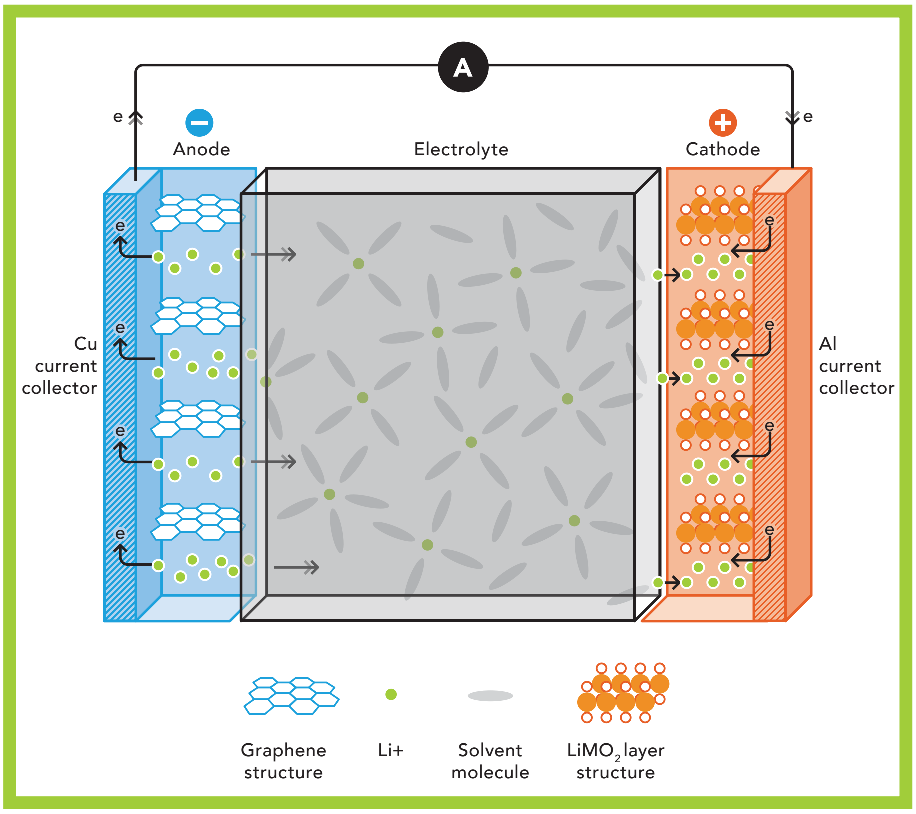
The positive electrode half-cell reaction is:

$$LiFe(II)PO_4 \quad \text{(arrows)} \quad Fe(III)PO_4 + Li^+ + e^- \qquad \text{(Equation 3.1)}$$

The negative half-cell reaction is:

$$xLi^+ + e^- + xC_6 \quad \text{(arrows)} \quad xLiC_6 \qquad \text{(Equation 3.2)}$$

FIGURE 3.1
Schematic of a lithium ion (Li-ion) battery during charge and discharge.



The energy and power density of the battery depends on the choice of materials used for the electrodes and the electrolyte, as well as the interface area between the components. Li-ion batteries are produced in different sizes for a broad range of applications, supplying power ranging from a few W to hundreds of kW. Current lithium ion technologies are targeted at consumer electronics, where high energy density and short charge / discharge times tend to be the most significant figure of merit. In grid scale applications, other factors dominate, such as long cycle life, good thermal stability, high current rate and endurance. Reassessing the important figures of merit significantly changes the choice of chemistry utilised for grid scale storage. Materials with great stability, such as the polyanionic frameworks ($LiFePO_4$ and Li_2FeSiO_4), become much more attractive, as well as sodium ion materials.

Na-ion batteries operate in a similar way to Li-ion batteries, but use sodium ions as the charge carriers. Although electrode materials and electrolytes already exist, the technology of Na-ion batteries is still at an early stage of development, compared with Li-ion batteries, which were first commercialised by Sony in 1991. The increase of interest can be demonstrated by the exponential rise in number of publications, climbing from 30 in 2009 to 580 in 2014.

3.2. Application to grid-scale storage

Table 3.1 gives the best current estimates of approximate performance / cost requirements for commercial Li-ion batteries. The depth of discharge and temperature will affect lifetime, but these parameters are not yet defined unequivocally. The advantages of Li-ion batteries over other battery technologies are: high energy density (400-550 Wh / L), high voltage (>3 V), high efficiency (>93 %) and an absence of memory effects, together with low maintenance and relatively low self-discharge. The memory effect seen in batteries corresponds to a reduction in the working voltage observed by repeated charge / discharge cycles, where the battery appears to 'remember' the depth of discharge from the previous cycle, leading to a reduction in battery capacity. This can have severe consequences on the durability and safety of battery systems. A Li-ion battery for the grid consists of arrays of battery cells connected into a parallel-series combination, packed into a module with a battery management system (one modular battery can deliver up to a few MW of power and a few 100's of kWh of energy). A battery-based system is able to respond quickly, in the order of tens of milliseconds.

TABLE 3.1
Table of performance and cost of Li-ion batteries.

Characteristics	Values
Specific energy, battery cell	120-200 Wh / kg
Energy density, battery cell	400-550 Wh / L
Specific power	750-2,000 W / kg
Power density	1,000-4,000 W / L
Calendar life	5-15 years
Cycle life	3,000-6,000 cycles
Cost of a battery pack	300-500 $ / kWh, target cost: 100 $ / kWh

A lithium ion battery (10 MWh) was installed in 2014 in Bedfordshire for a two-year trial, operated by UK Power Networks. This consists of 3,000 units of Li-ion batteries, achieving a round trip efficiency of 95 %; a predicted 10 year lifetime, with 4,000 cycles for one battery pack and producing 400-550 Wh / L. Another example in the UK was the first Li-ion battery connected to the grid in Orkney to balance power demand across the Scottish islands.

Although Li-ion batteries offer considerable advantages, they are currently still too expensive for most grid applications, but the current cost of 250 $ / kWh may drop to 150 $ / kWh in the next five years. The cost depends on a number of factors, including the cost of the raw materials required to manufacture the electrodes, the manufacturing process, the cell fabrication process and the market demand compared with the production capacity. According to the NEC project in Maui Hawaii, the largest component cost for the battery itself was the Li-ion cells, though the cost breakdown is not provided [4]. It is interesting to note that in the transport sector, which has seen a parallel change to lithium battery technology, the cost has dropped faster and further than predicted, caused largely by a worldwide overcapacity compared with the market size. The current cost of Li-ion battery packs for transport is approximately 300 $ / kWh, whereas 500 $ / kWh was widely anticipated.

3.2.1. Anodes

Graphite continues to be the dominant anode in Li-ion batteries. Efforts are underway to replace it with silicon, which would increase energy density. Cells with titanate based anodes are also in the market for grid applications because they offer superior safety, high rate and high cycle life compared with graphite, but at the expense of energy density.

For most materials, a solid electrolyte interphase (SEI) is formed between the anode and the electrolyte during the initial charging step of the battery through degradation of the electrolyte and is essential in passivating the surface, preventing further electrolyte reduction. However, if a poor SEI film is formed at graphitic electrodes, this can significantly restrict battery performance. Therefore understanding SEI formation is crucial, as the SEI affects the performance of Li-ion batteries in terms of power, capacity and cycle life. The main strategy to improve this is through the use of additives which enhance the properties of the SEI, thus avoiding electrolyte degradation and the loss of lithium capacity.

> Understanding the formation of the solid electrolyte interphase is crucial, as it affects the performance of Li-ion batteries in terms of power, capacity and cycle life.

3.2.2. Cathodes

For cathodes, there is a focus on utilising low cost elements such as manganese and iron as the basis of the materials to replace costly and toxic elements, such as cobalt. Lithium manganese oxides and related materials containing other transition metals such as nickel, are already in use e.g. $Li(Mn_xCo_{1-2x}Ni_x)O_2$ with $x = 0.4$ or 0.45 [5]. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, commonly denoted as LNCA, has also recently been used for grid applications. Many of the lithium batteries for grid scale applications employ lithium-iron phosphate ($LiFePO_4$, referred as LFP). This material offers better safety and higher cycle life, at the expense of lower specific energy (typically 150 mAh / g) and voltage, having a flat charge / discharge profile at an intermediate voltage of 3.45 V vs. Li/Li^+, compared with ~200 mAh / g and 4 V for the layered lithium transition metal oxides.

Most of the manufacturers of Li-ion batteries for the grid use LFP as a cathode material, for example the patented Nanophosphate® [6] developed at the Massachusetts Institute of Technology, or Saft's Super-Phosphate™ (Serial number 79081342). Alevo's GridBank™ batteries (Serial Number: 8584474) provide 2 MW / 1 MWh and are based on LFP and graphite. Tesla and Panasonic are jointly entering the grid market with their so-called 'Gigafactory', currently under construction in Nevada, USA. Their cathode of choice for grid storage is $LiNi_xMn_yCo_zO_2$ ($x+y+z=1$), denoted NMC. Interestingly, this is different from the cathode that Tesla uses for its automobile batteries, the material in this case being LNCA. This is an excellent example of tailoring battery chemistry to the specific requirements of its application.

3.2.3. Electrolyte

To overcome the safety issue in Li-ion batteries, polymer electrolytes have been developed. These are safer than their liquid counterparts, since they are not flammable. The polymer layer must be thin, on the order of 10-100 µm, because the conductivity is lower than liquids by at least an order of magnitude. An example of the application of this technology is the solid-state battery, DryLyte™ (Serial Number 86098778) [7], developed by Seeo for stationary energy storage, providing an energy density of about 220 Wh / kg [8]. The technology consists of a block copolymer solid electrolyte in which one soft layer of polymer conducts ions and one hard layer of polymer forms a barrier between the electrodes, avoiding short-circuits caused by dendrites. Another polymer electrolyte-based battery is the lithium ion SuperPolymer® battery [9] manufactured by Electrovaya that could offer up to an energy density of 450 Wh / L with chemistries based on lithium metal oxide materials [10].

3.2.4. Sodium-ion batteries

Na-ion batteries represent a potentially attractive storage technology at a lower cost for grid scale applications. The price for Na_2CO_3 (120 $ / ton) is approximately 30 times lower than Li_2CO_3 (4,000 $ / ton). These are typical raw materials for manufacturing cathodes for Na-ion and Li-ion batteries, respectively. Sodium is much more abundant than lithium in the Earth's crust (23,600 ppm of Na compared with 20 ppm of Li) [11] and 105 ppm is contained in sea water, making its resources almost unlimited. This is of even greater importance, given the fact that the majority of lithium resources are restricted to only a very select number of locations. However, there are some drawbacks. The electrochemical standard potential of Na^+/Na is 0.34 V higher than that of Li^+/Li and the sodium atom is three times heavier than the lithium ion (23 g / mol compared with 6.9 g / mol) [12]. As a consequence, the gravimetric and volumetric energy densities are theoretically lower for a sodium system than those for a directly equivalent lithium system. However, given that lithium systems do not in practice attain theoretical performance, it may be possible to achieve similar energy densities for both lithium and sodium.

In addition, Na-ion batteries present some technological challenges. As Na^+ has a larger ionic radius than Li^+, the host electrode materials require enough interstitial space to allow ion insertion / extraction. In some cases this can be advantageous, as in layered transition metals where the larger gap between transition metal layers suppresses irreversible structural transformations which have also been seen to activate elements with poor electrochemical performance such as chromium. Although graphite is commonly used for Li-ion batteries, graphite anodes show poor performance for Na-ion batteries as the interstitial space is too narrow for sodium atoms. The anode could consist of Na metal, but the melting point is rather low (97 °C), posing a possible safety risk. As hard carbons have a wider interstitial space, sodium intercalation is possible; thus, they have become the anode material of choice, despite their low surface area, which compromises rate, i.e. power. Some research has been carried out on transition metal oxides for anode materials, mainly TiO_x and VO_x, but their voltage is higher, reducing what is already a lower cell voltage than Li-ion batteries.

The non-aqueous electrolytes commonly used for Na-ion batteries are $NaPF_6$ salts in carbonate ester solvents. When using hard carbons, the electrolyte spontaneously decomposes at the anode to form the SEI layer, protecting the carbon from further reaction with the electrolyte and permitting reversible intercalation of the sodium ions. An alternative route is the use of aqueous electrolytes.

Recently, Na-ion batteries, Aqueous Hybrid Ion (AHI™), have been commercialised by Aquion Energy for grid scale applications. The battery chemistry uses an activated carbon anode, a $NaMnO_2$ cathode and a neutral pH aqueous based electrolyte containing Na_2SO_4 [13]. At the moment, the cost of such a battery is 250 $ / kWh, similar to lead-acid batteries (200-300 $ / kWh). The technology is claimed to deliver a round-trip energy efficiency of 85 % at 5,000 cycles over 5-15 years, but this has yet to be verified.

Cathode materials for Na-ion batteries serve as a host for Na to be inserted / extracted. As is for Li-ion, the focus is on low cost elements, iron and manganese oxides, phosphates or sulphates, for example $Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$, $Na_2FeP_2O_7$ and $Na_2Fe_2(SO_4)_3$ [14]. The benefit of the oxyanions is, as with Li-ion systems, better safety as the oxygen is trapped by a strong covalent bond to the P or S and therefore cannot be released as easily as in an oxide. However, the major disadvantage is lower volumetric energy density.

The sodium-ion batteries that are currently being developed use a large range of layered oxide active materials for the cathode and hard carbon as the anode, along with organic electrolytes [15]. An energy density of 340 Wh / L is predicted to be achieved, compared with 250-260 Wh / L for commercial LFP [16].

3.3. Lithium-ion battery research needs for grid scale storage

3.3.1. New cathode materials

A lot of research has been carried out on cathode materials with the aim of finding an electrode with high rate capability, high charge capacity and high operating voltage. Although many cathode materials look promising, they often suffer from poor kinetics, poor mechanical stability or are incompatible with the electrolyte. Research on new types of electrode materials needs to continue, along with pursuing strategies to overcome the key lifetime and safety challenges, while also lowering cost. This can be achieved by examining alternative chemistries such as polyanionic materials, e.g. LFP, or by considering alternative preparation methodologies. For example, materials with promising theoretical properties which show limited bulk practical electrochemical activity due to poor electronic and ionic conductivity, can be activated by the synthesis of nanoparticulate equivalents. This reduces the limiting length scales and therefore enhances performance. Besides developing nanometre scale materials, other strategies to improve electrode performance include adjusting the electrode formulation and electrode coatings.

3.3.2. New anode materials

The typical electrode material for Li-ion batteries is graphite, owing to its low potential versus the lithium metal electrode, maximising the energy of the battery cell. However, poor safety and limited lifetime are the two main obstacles to achieve good performance of the battery for the grid. Lithium titanate (LTO) is an alternative electrode material that has some advantages compared with graphite. LTO has a working potential of 1.3 V higher than graphite, thus avoiding lithium deposition and electrolyte decomposition. Additionally, this material undergoes negligible volume changes on cycling, making it extremely stable. Therefore LTO can retain most of its original capacity after hundreds of cycles, a quality that can lead to a longer lifetime in batteries. However, high working voltage also means lower energy density. This suggests that the greatest needs when considering anodes for grid storage are cycle life and safety, both of which can be addressed by considering elevated potential alternatives to graphite. Another promising electrode material for anodes is silicon, capable of storing about 10 times more lithium ions per unit volume than graphite, which in turn helps to drive the costs down. Unfortunately, the significant volume change during lithiation / delithiation causes rapid capacity fading. The challenge for silicon anodes lies in improving the cycle life through a Si electrode design that addresses the volume change problem. If the cycle life of Li-ion cells using silicon in anodes is greatly improved in consumer and automotive applications, then it could be considered for the grid.

> Silicon, a new anode material, is capable of storing about 10 times more Li ions per unit volume than graphite, driving down battery cost. However, significant volume change during lithiation / delithiation causes rapid capacity fading.

3.3.3. New electrolytes

Carbonate ester solvents are commonly used in Li-ion batteries, but alternate electrolytes could ensure better stability. Research on the electrolyte could improve not only conductivity but also safety and stability. New battery chemistries should emerge, inducing new electrolytes and compositions. The understanding of the SEI formation is also essential to maintain lithium transport through the electrolyte between the two electrodes. Ionic conductivity and voltage stability are the key properties of the electrolyte.

> Research on new electrolytes could improve not only conductivity but also safety and stability.

3.3.4. Cost reduction

We also need to consider the energy embodied in order to build a grid scale battery, relating to the cost. The embodied energy corresponds to the total amount of energy required to build and deliver the technology, from the extraction of raw materials, such as lithium, to the manufacture and installation of the finished device [11]. It was revealed that the Li-ion battery can store on average 10 times the embodied energy upon achieving 6,000 cycles during its lifespan, compared with only 2 times for a lead-acid battery. This study therefore shows that research should focus on extending the cycle life, but the battery research community is currently focused on improving storage capacity and power.

> Research should focus on extending the cycle life, but the battery research community is currently focused on improving storage capacity and power.

3.3.5. Battery degradation

Li-ion batteries undergo changes while operating, for example the SEI layer growth can increase depending on factors such as temperature, the storage state-of-charge (SOC) or charging and discharging processes. These stress factors will impact on the cell capacity and the inner resistance of the battery. Also, maintaining a battery at 100 % SOC results in a faster degradation rate than at a lower SOC. Mechanisms of ageing behaviour of Li-ion batteries, influenced by different factors such as SOC, charge /discharge rate and depth of discharge need further investigation, as this impacts their efficiency and lifespan.

> Maintaining a battery at 100 % SOC results in a faster degradation rate.

3.4. Sodium-ion battery research needs for grid scale storage

3.4.1. Negative electrode materials

Although graphite is commonly used as an anode in Li-ion batteries, sodium insertion into graphite is not reversible. One of the major problems for the application of Na-ion batteries is the lack of a suitable negative electrode material. Some alternative materials have been found, such as hard carbons with a specific capacity of 300 mAh / g. Alloys and conversion materials have also been the focus of significant research. The electrode performance of hard carbons needs further optimisation. It is clear that the discovery of high capacity, reversible negative electrode materials would represent a major breakthrough in this area. Additionally, understanding the SEI layer in sodium ion systems is key, as this is far less understood than for the anodes of Li-ion equivalents. Mechanistic studies are needed to understand the formation of the interphase at the electrode / electrolyte interface, having a major influence on cycle life.

> It is clear that the discovery of high capacity, reversible negative electrode materials would represent a major breakthrough in this area.

3.4.2. Positive electrode materials

Some options for metal-oxide based cathode materials already exist and currently the most significant challenge is maintaining cycle life without compromising capacity. It may be possible to take advantage of the progress made in Li-ion batteries to inform this development. To date, no single system has surfaced as the dominant option and the scope for new discoveries is extremely wide.

3.4.3. Electrolytes

Electrolytes for Na-ion batteries have so far received a limited research focus from the battery community. Much greater attention must be paid to this area in order to establish electrolyte options of a quality comparable to those used for Li-ion systems.

4. Aqueous-based Batteries

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Batteries based on aqueous electrolytes are a large and well-established class of energy storage devices. Their relative ease of manufacture makes them among the cheapest and safest class of battery, but they suffer the disadvantage of lower cell voltages than their non-aqueous counterparts. Lead acid technologies dominate global sales in this class and a variety of chemistries based around a nickel positive electrode have widespread industrial applications. Looking to future grid applications, new materials and configurations are needed with new NiFe and so-called "rocking-chair" batteries offering the best chance for step changes in cost and performance.

4.1. Introduction to the technology

In general, aqueous batteries have the advantage of ease of manufacture (no need for a controlled inert atmosphere). Related to this, they have lower costs than their high temperature and non-aqueous equivalents. However, they were not specifically designed for grid connection and research is needed to either redesign them, or to develop new aqueous-based chemistries. Their principal disadvantage is that they have lower cell operating voltages (1.2 V for NiCd, 2 V for lead acid). This means that more cells need to be connected in series to achieve the overall operating voltage, for connection to an inverter and step-up transformer, typically 600 V.

> Aqueous batteries are easier to manufacture than their high temperature and non-aqueous equivalents, therefore they have lower costs.

The aqueous electrolyte generally gives them favourable safety features, especially with regard to flammability and thermal runaway during charge / discharge. Other important characteristics, such as efficiency, lifetime, power to energy ratio (MW / MWh) and use of scarce materials, vary considerably and are considered on a case-by-case basis.

At present, lead acid cells are the most common aqueous-based battery system and account for the majority of battery sales worldwide. It was reported that during 2010, the use of lead acid batteries in China achieved a 75 % connection rate to all new photovoltaic systems; likewise, during 2008, lead acid technology held 79 % of the US rechargeable battery market share.

In this chapter, we consider a number of promising aqueous-based batteries, assessing them for development as grid storage devices. Each section is devoted to a different class of aqueous battery, which outlines their general characteristics and gives the basic operating chemistry, using the following convention:

1. Negative electrode (anode) discharge reaction left to right, as written.

2. Positive electrode (cathode) discharge reaction left to right, as written.

An assessment of either current deployment or grid connection potential is then given. Here we are assessing the possibility of creating batteries of up to ~1 MW / 1 MWh, capable of a ~10 year life cycle (approx. 3,000-5,000 charge / discharge cycles). Finally, we outline the research priorities needed for aqueous batteries as a whole.

4.1.1. Lead acid batteries

The oldest example of a practical rechargeable battery was developed by Gaston Planté in 1859, using lead and sulphuric acid [17]. This technology dominates the global market for small to medium scale electrochemical energy storage applications. They are widely used in automotive applications, for engine starting, lighting and ignition.

In their simplest form, lead acid batteries consist of metallic lead as the negative electrode, lead dioxide as the positive electrode and a dilute solution of sulphuric acid as the electrolyte. During discharge, the metallic lead (negative) electrode is oxidised to Pb^{2+}, which precipitates as $PbSO_4$, as follows:

Pb (two-way arrow) $Pb^{2+} + 2e^-$ $E_0 = -0.13$ V (Equation 4.1)

$Pb^{2+} + SO_4^{2-}$ (one-way arrow) $PbSO_4$ (Equation 4.2)

The positive lead oxide (PbO_2) electrode is reduced to Pb^{2+} and, subsequently, a $PbSO_4$ precipitate:

$PbO_2 + 4H^+ + 2e^-$ (two-way arrow) $Pb^{2+} + 2H_2O$ $E_0 = 1.46$ V (Equation 4.3)

The most common problem in the lead acid battery is the negative electrode sulphation, which is the formation of nearly insoluble crystals of lead sulphate. On charging, these crystals only regenerate to a minimal extent, adversely affecting cell efficiency and lifetime. Advanced lead acid batteries replace the Pb electrode with either carbon or a composite carbon / Pb electrode. This gives enhanced cycling, due to reduced sulphation at the negative electrode.

4.1.2. Nickel based batteries

Nickel is used as the positive electrode for a variety of alkaline type batteries. In all of these cases, the active material is nickel oxy-hydroxide (NiO.OH), which is formed from nickel hydroxide during battery charging. There are a variety of materials used for the negative electrode, giving different classes of Ni-based batteries. The most important in the market are nickel cadmium (NiCd), nickel metal hydride (NiMH) and nickel iron (NiFe).

The respective negative electrode chemistries are:

NiCd: $Cd + 2OH^-$ (two-way arrow) $Cd(OH)_2 + 2e^-$ (Equation 4.4)

NiMH: $MH + OH^-$ (two-way arrow) $M + H_2O + e^-$ (Equation 4.5)

(M is typically an AB_5 intermetallic, where “A” is a rare earth such as La, Ce, Nd and “B” can be Ni, Co, Mn, Al).

NiFe: $Fe + 2OH^-$ (two-way arrow) $Fe(OH)_2 + 2e^-$ (Equation 4.6)

During discharge, the general equation of the nickel (positive) electrode in alkaline media is:

$NiO.OH + H_2O + e^-$ (two-way arrow) $Ni(OH)_2 + HO^-$ (Equation 4.7)

When charging NiFe batteries, water can be decomposed yielding hydrogen, a process that reduces cell efficiency. Mitigation of hydrogen production has been traditionally achieved by modification of the iron electrode formulation, using the addition of components such as sulphur or bismuth. These increase the activation energy for water decomposition [18]. NiFe cells use strongly alkaline solutions of potassium and lithium hydroxide and selected additives, such as potassium sulphide, to prevent electrolyte decomposition.

4.1.3. Copper-Zinc batteries

Invented by John Frederic Daniell in 1836, the CuZn battery operates at a net cell potential of 1.08 V [19]. It consists of two metal plates, each in its own electrolyte, connected through a semi-permeable membrane. Cumulus Energy Storage is undertaking the commercial development of a rechargeable copper-zinc battery. The negative electrode - the anode - is composed of metallic zinc in an aqueous solution of zinc sulphate. During cell discharge, the elemental zinc is oxidised to Zn(II):

Zn (two-way arrow) $Zn^{2+} + 2e^-$ (Equation 4.8)

Likewise, the positive electrode is metallic copper in an aqueous solution of copper sulphate. During cell discharge, Cu(II) is reduced to metallic copper:

$Cu^{2+} + 2e^-$ (two-way arrow) Cu (Equation 4.9)

4.1.4. Aqueous electrode insertion or “Rocking-chair” batteries

“Rocking-chair” batteries are the aqueous analogue of the widely used insertion electrode based Li-ion batteries. The positive and negative materials are usually host-layered structures to facilitate intercalation of the lithium ions. During charge and discharge, lithium ions diffuse back and forth between the electrodes through the electrolyte, with the corresponding flow of electrons in the external circuit. Dahn’s group developed the first aqueous Li-ion battery in 1994 with VO_2 as negative electrode and the spinel $LiMn_2O_4$ as positive electrode with a 5 M $LiNO_3$ electrolyte [20]. Other research groups have subsequently used different materials very similar to non-aqueous Li-ion technology [21]. The company Aquion Energy is commercialising this concept.

Typical electrochemical reactions are:

Li_xVO_2 (two-way arrow) $VO_2 + xLi^+ + xe^-$ (Equation 4.10)

$Li_{1-x}Mn_2O_4 + xLi^+ + xe^-$ (two-way arrow) $LiMn_2O_4$ (Equation 4.11)

4.1.5. Metal-air batteries

In order to achieve greater energy densities, aqueous-based battery systems that use cell architectures more akin to that seen in fuel cells are being developed. The negative electrode consists of a metal and the positive electrode allows interaction between the metal ions and atmospheric oxygen. The challenge is to produce rechargeable (or secondary) batteries.

Zinc air batteries: Primary zinc-air cells are a fairly mature technology that has found commercial applications in medicine and telecommunications. As with other metal-air cells, a major driver for development is their high theoretical energy density (1,086 Wh / kg, including oxygen) [22]. The compatibility of zinc with an aqueous alkaline electrolyte allows for substantially reduced manufacturing costs in comparison with non-aqueous based cells. However, the development of electrically rechargeable zinc-air cells has been hindered by the propensity of zinc to form dendrites upon repeated charge / discharge cycling, as well as their low output power. A further drawback of aqueous alkaline electrolytes is the absorption of carbon dioxide by the solution, producing insoluble, electrode-blocking compounds that reduce electrolyte conductivity and impede cell performance. As a consequence, the process of air purification needs to be considered alongside cell design. Improvements in performance require the identification of suitable robust catalysts and electrolyte additives to prevent dendrite growth.

Iron air batteries: An alternative cell chemistry that has received attention of late is the iron-air cell that also operates in an aqueous alkaline electrolyte. Iron-air cells do not exhibit the same stripping / redeposition problem seen in zinc-air cells, but have a lower theoretical energy density of 764 Wh / kg and electrically rechargeable cells exhibit relatively low energy efficiencies (ca. 35 %) [23]. As with zinc-air cells, the development of a more efficient oxygen electrode is required.

4.2. Application to grid scale storage

4.2.1. Lead acid batteries

Lead acid batteries have been used for grid scale energy storage in California (10 MW / 40 MWh), Hawaii (15 MW / 3.75 MWh), Puerto Rico (20 MW / 14 MWh) and Germany (8.5 MW / 8.5 MWh), among others. In the UK, SSE have installed and operate a 1.3 MW / 6.3 MWh YUASA lead acid battery in their Lerwick power station, although only 3 MWh of the capacity is used. Their target lifetime is 5 years / 1,500 cycles. Interestingly, this battery replaced an already installed NaS battery, which had never been operated due to safety concerns.

Since the lead acid battery has an operating voltage of 2.1 V and a typical capacity of 40 Ah, it is necessary to use 285 cells in series to obtain a system with approximately 600 V and 42 cells in parallel to obtain 1 MWh, resulting in a system with 11,970 cells (c.f. a car battery which has 6 cells in series with 12.6 V operating voltage and 504 Wh). Lead acid batteries have self-discharge rates of 4-20 % per month, a typical cycle efficiency of ~63-90 %, are fabricated from low cost materials and can be easily recycled after use. However, the low cycle life (~1,000) and high maintenance costs elevate the life-cycle cost. In addition, material toxicity is a concern.

Three important variants of lead acid battery design are: deep cycle, absorbent glass mat / gel vs. flooded and advanced lead acid. While most lead acid batteries are designed to provide short bursts of power for engine cranking, deep cycle batteries have thicker electrodes and additives, such as antinomy, to give enhanced depth of discharge, typically to 30-45 %. The thicker electrodes increase the energy density, while the antinomy increases the mechanical strength of the electrodes, enabling them to withstand the deeper discharge. The “flooded” design consists of the electrodes dipped in a tank of excess electrolyte. This design has largely been abandoned due to high maintenance costs and reduced energy density for starter and traction batteries. The use of absorbent glass mats as separators enhances power density, reduces maintenance and increases lifetime. Advanced lead acid batteries replace the negative lead electrode with either a Pb / carbon composite, or a pure carbon electrode. This has the effect of reducing sulphation of the negative electrode and increasing cycle life. However, this also reduces energy density.

> Advanced lead acid batteries use pure carbon or Pb / carbon composites for the negative electrode. This reduces sulphation and increases cycle life, while reducing energy density.

4.2.2. Nickel based batteries

NiCd batteries: Research efforts in this area are centred on improving their energy density and cycle life, alongside preventing the reactions that result in self-discharge. An example of this technology being used for grid support is the system developed by GVEA that uses ~14,000 NiCd cells, providing backup power of 27 MW for up to 15 minutes. This system has been in operation since 2003. The toxicity of cadmium, as well as the recent discovery that NiCd cells are associated with higher CO_2 and SO_2 emissions during their production, compared with lithium-based cells [24], are major drawbacks of NiCd technologies.

> Cadmium toxicity and higher emissions of CO_2 and SO_2 are major drawbacks of NiCd technologies.

NiMH batteries: NiMH cells are characterised by energy densities of around 250-330 Wh / L, a specific energy up to 100 Wh / kg and are limited to 1,000 cycles. Compared to NiCd cells, they can deliver roughly twice the number of cycles, but they are associated with a low energy density. Without substantial improvements, the restricted cycle life of NiMH renders them unsuitable for large-scale grid connected applications.

> The restricted cycle life of NiMH renders them unsuitable for large-scale grid applications.

NiFe batteries: There has been renewed interest in iron-based electrodes and NiFe cells are well known for their long cycle life. They were successfully commercialised in the early 20th century, but fell out of favour with the advent of cheaper lead acid cells and subsequently received little attention with regards to development. This technology could provide a cost effective solution for large-scale energy storage applications, due to its relative environmental friendliness, longevity and tolerance for electrical abuse. For example, cells can recover from over- charge / discharge, or relatively long idle periods. The relative abundance of the raw materials required to produce NiFe cells is another aspect favouring its use. Nickel and iron are among the most abundant elements in the Earth's crust and less abundant elements included in the cell (such as bismuth) are used in relatively small proportions, therefore NiFe cells have the potential to be manufactured at relatively low cost.

> NiFe technology could provide a cost effective solution for large-scale energy storage applications, due to environmental friendliness, longevity and tolerance for electrical abuse.

4.2.3. Copper-Zinc batteries

The relatively high internal resistance of these batteries means that only a moderate current can be taken from them. Deposition of copper in places other than the copper electrode is a problem that renders the battery inactive. In addition, when the battery is not in action, copper ions diffuse through the membrane to reach the zinc side of the battery. Copper is then deposited on the zinc plate as black cupric oxide, CuO, impairing the performance of the battery. This process is usually controlled by deactivating the battery when not in use. Notwithstanding these difficulties, the CuZn battery is a simple, safe and potentially cost-effective device with potentially important grid applications. Cumulus Energy Storage is undertaking the commercial development of a rechargeable copper-zinc battery. They aim to develop safe, low cost battery systems with capacities in the region of 1 to 100 MWh.

> The CuZn battery is a simple, safe and potentially cost-effective device with potentially important grid applications.

4.2.4. Electrode insertion batteries

Aqueous intercalated batteries employ environmentally friendly materials and display no memory effects. However, the complexity of the electrochemical and chemical reactions during the insertion / de-insertion processes in aqueous systems makes them very challenging, compared with organic-based batteries. A clear limitation in these batteries is the restricted stable voltage window of aqueous electrolytes. The decomposition of the electrolyte occurs at 1.23 V and involves H_2 or O_2 gas evolution. This potential defines the stable operating voltage window in aqueous systems, although it is very low compared with that of the organic-based systems (3.0 V for Li-ion batteries), indicating a lower energy density storage (75 Wh / kg), but one which is still larger than that of NiCd batteries (25 Wh / kg). There are many side reactions that limit their performance and cycle life. The main drawbacks of this technology are: (i) the reaction of molecular hydrogen or oxygen on electrolyte decomposition, (ii) proton (H^+) co-intercalation into the host electrode, (iii) reactions between electrode material and water or residual molecular oxygen and (iv) the dissolution of electrode materials [25]. Nevertheless, different approaches have been used to overcome these issues and commercial systems are already in the market.

Aquion Energy use a cubic spinel $LiMn_2O_4$ as the positive electrode and an activated carbon / $NaTi_2(PO_4)_3$ composite as a negative electrode. Their devices are able to work for thousands of cycles, without significant capacity loss. Their smallest product, the Aquion S-Line Battery Stack with eight batteries in series, has a nominal energy of 2.4 kWh at 20 hour discharge at 30 °C, with a round trip efficiency of ~85 %. The discharge curve appears more similar to that of a supercapacitor than a conventional battery and loss of voltage with discharge poses problems in interfacing with power electronics.

4.2.5. Metal-air batteries

Eos Energy Storage is in the process of commercialising zinc-air systems that use a hybrid zinc electrode and neutral pH aqueous electrolyte that avoids several of the problems historically encountered in zinc-air chemistry. They are developing a grid scale (1 MW / 6 MWh) system that has a round-trip efficiency of 75 % and is projected to last for 10,000 charge / discharge cycles. The power to energy ratio is perhaps indicative of the reduced power handling of this battery class.

4.3. Research needs for grid scale storage

Research into many aspects of aqueous battery technology is essential and although there are some important commercial developments, research is not as developed as for non-aqueous Li-ion. However, aqueous technology is potentially the cheapest form of electrochemical storage and has clear safety advantages. The US DoE Global Energy Storage Database (http://www.energystorageexchange.org/) shows relatively few aqueous battery demonstration projects and it is therefore difficult to assess their true potential. Much more data is needed on this aspect.

> Aqueous technology is potentially the cheapest form of electrochemical storage and has clear safety advantages.

In research terms, many aqueous-based battery technologies are regarded as being “mature”, e.g. Pb acid, NiCd and NiMH. Recent progress has been incremental and may be better when performed in an industrial context. In order to improve lead acid battery performance, the use of carbon in combination with Pb, or even a carbon-only electrode, has been proposed for the negative electrode, showing promising performance for grid applications. This kind of modification increases the energy output and reduces the sulphation issue, increasing the cycle life to ~3,000 cycles. New materials for the electrode grid must also be considered. It should always be remembered that the use of lead acid batteries in grid applications is already well-established and that they are quite commonly the default battery for supporting renewables such as PV due to cost, safety and availability.

Over the past 20 years, the hydrogen storage community have developed a large number of new metal hydrides for hydrogen storage. But little of this research has transferred into the battery community, either in the UK or globally. Given UK strengths in these classes of materials, there is an opportunity to evaluate new metal hydrides as battery electrodes in NiMH batteries.

> Given UK strengths in metal hydrides, there is an opportunity to evaluate them as battery electrodes in NiMH batteries.

Short- to medium-term battery developments, for deployment in 1 - 10 years, should concentrate on relatively simple battery structures such as NiFe and CuZn, which were not originally designed for grid connection but which could be easily adapted for this role. Both have the advantage of utilising relatively cheap, safe and easily recyclable materials.

> Due to their extended cycle life, lower toxicity and lack of memory effects, NiFe is a highly promising technology, scalable from domestic to grid, but requiring a collaborative electrochemistry and engineering approach.

Due to their extended cycle life (running into thousands), lower toxicity and lack of memory effects, NiFe cells are probably the most promising of all Ni-based technologies for large scale energy storage. The improvement of these batteries hinges on increasing their round-trip efficiency by suppressing unwanted hydrogen evolution. Finally, the low power density of these batteries can be increased by improving the kinetic characteristics of the inter-conversion of Fe(0) to Fe(II) that takes place during the charge and discharge of the battery. There is already interesting research in this area, in particular using FeS and a variety of other electrode and electrolyte combinations. It is surprising that no serious attempts have been made to apply the techniques of nanoscale engineering to improve the power handling of this battery. Also, a survey of the literature shows little fundamental understanding of the chemical effects of additives. The Ni electrode may be regarded as a mature technology, as it has been commercialised and industrially optimised over a period of decades for use in NiCd and NiMh batteries. NiFe is a highly promising technology, scalable from domestic to grid, but requiring a collaborative electrochemistry and engineering approach. Even if the power handling cannot be improved, it is easy to conceive that their low cost and long cycle life properties will make them ideal hybrids with other technologies for grid applications, such as lithium titanate batteries.

CuZn batteries need significant improvements in membrane technology, in terms of reduced thickness and selectivity, before it can act as a truly rechargeable battery. Unless this problem is solved, the maintenance costs may be problematic, as this would entail periodic draining and purification of the electrolyte, as well as possible membrane replacement. Again, these batteries have received little attention at the fundamental level to date, with very few papers appearing in the scientific literature.

> CuZn batteries need significant improvements in the thickness and selectivity of its membrane technology, before it can act as a truly rechargeable battery.

Finally, in the long term (>10 years), the "rocking-chair" battery offers a promising new class of batteries. New and novel combinations of electrodes, coatings and separators need to be explored.

> In the long term, the "rocking-chair" battery offers a promising new class of batteries.

5. Supercapacitors

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Supercapacitors bridge the power and energy gap between dielectric capacitors and Li-ion batteries. With a long cycle life, supercapacitors are attractive for meeting electrical peak demands in the grid, but research and development is needed to tailor both electrode materials and electrode structure for specific grid scale storage applications. The core challenges for supercapacitors are the need to reduce cost to make widespread deployment feasible and to increase energy density without sacrificing their distinctive high power density and long cycle life.

5.1. Introduction to the technology

Supercapacitors consist of a porous separator sandwiched between two electrodes, immersed in a liquid electrolyte (Figure 5.1). They store electrical charge by electrostatic adsorption of electrolyte ions in an electric double layer (EDL) at the electrode surface.

The capacitance, C, provided by an electrode is:

$$C=SA\varepsilon/d \qquad \text{(Equation 5.1)}$$

so that C increases with increasing electrode surface area, SA, and decreasing EDL thickness, d, and ε is the electric constant ε_0 (8.85 x 10^{-12} m^{-3} kg^{-1} s^4 A^2) times the relative dielectric constant of the electrolyte, ε_r.

In most commercial supercapacitors, high capacitance is provided by porous, high surface area (~2000 m^2 / g) activated carbon powders in the electrodes, which are produced by carbonisation of cheap raw materials such as coal, phenolic resin or coconut shell, followed by a high temperature “activation” process. Theoretically, activated carbon can provide up to 25 μF / cm^2 and 500 F / g per electrode, but usually less than 50 % is realised because of the parasitic mass of polymer binders (~10 vol%) and carbon-based electron conductivity enhancers (~5 %) that are required. The energy, E, is:

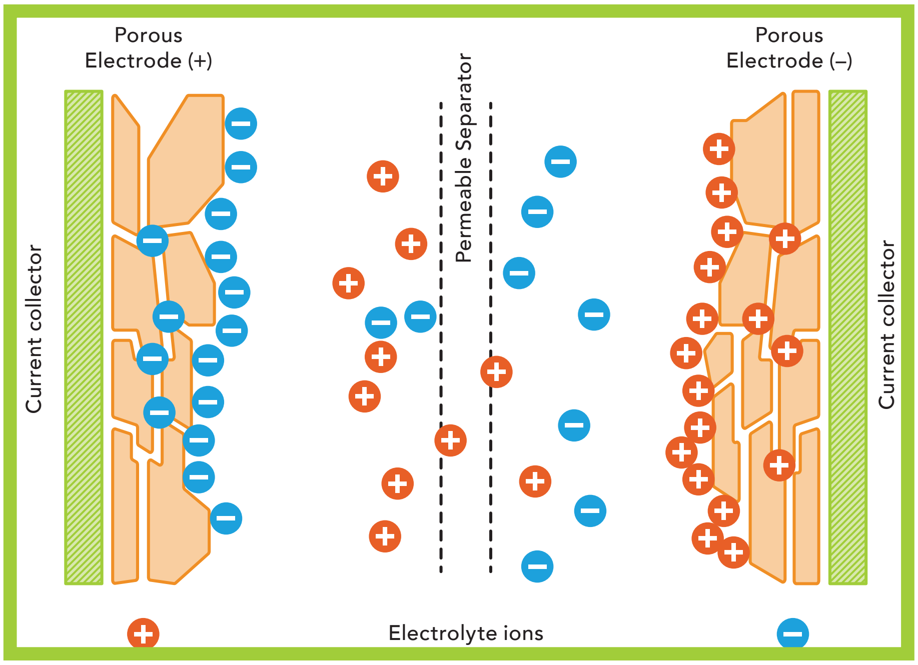
$$E=1/2\ CV^2 \qquad \text{(Equation 5.2)}$$

where V is the operating voltage. Consequently, commercial supercapacitors use organic electrolytes to maximise the operating voltage, up to ~2.7 V (c.f. ~1 V for aqueous electrolytes, to avoid electrolysis of the water). However, organic electrolytes have a low electrical conductivity (~0.02 S / cm) compared with aqueous electrolytes (~1 S / cm), undermining their power density, P:

$$P=V^2/(4R) \qquad \text{(Equation 5.3)}$$

where *R* is the internal resistance (the total resistance of all materials between the two current collectors in Figure 5.1).

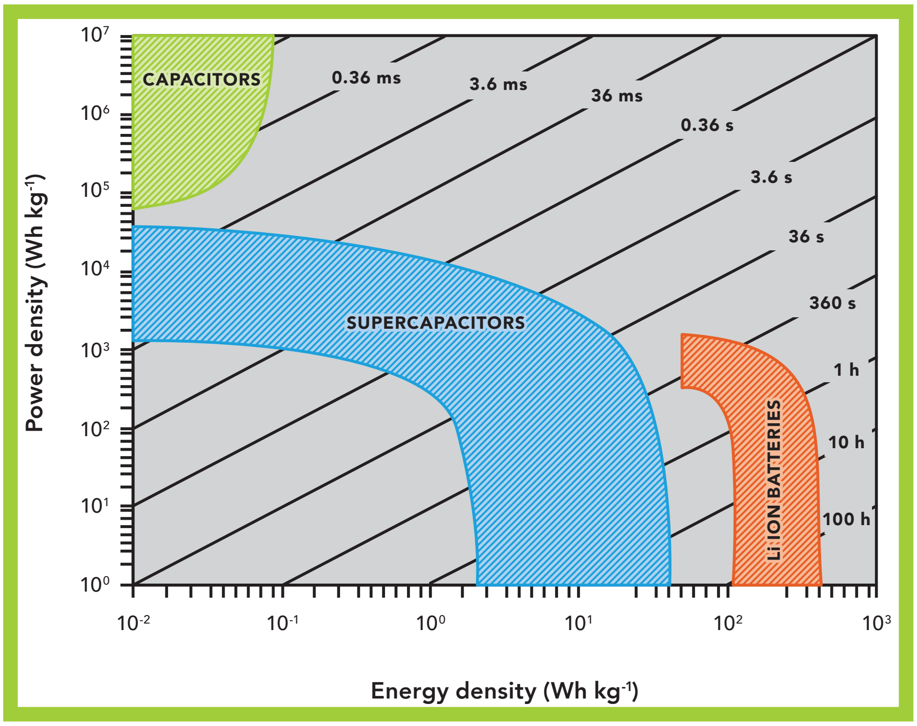
FIGURE 5.1
A schematic diagram of a supercapacitor in the charged state.



Faradaic surface reactions between the electrode and electrolyte that transfer electrons between oxidised and reduced species can provide pseudo-capacitance of 100-400 µF / cm^2. Pseudo-capacitors may include metal oxides, conducting polymers and functionalised carbon. Metal oxides may show a range of oxidation states and have high pseudo-capacitance (>1,000 F / g), but can be expensive and suffer from rapid fading, due to the strains associated with faradaic reactions.

Figure 5.2 shows a Ragone plot of the energy and power densities of Li-ion batteries,

FIGURE 5.2
Ragone plot of electrical energy storage systems.



supercapacitors and dielectric capacitors. Supercapacitors provide ~10 times higher power density than Li-ion batteries and a much higher energy density than dielectric capacitors. Supercapacitors have long cycle life (~105 cycles), do not suffer from thermal runaway and may operate from -40 to 65 °C.

5.2. Application to grid scale storage

Smart grids are designed to improve the reliability and tolerance to fluctuations of electricity transmission and distribution, thereby facilitating the integration of renewable energy generation. Although approximately 90 % of power outages only last two seconds or less, with 98 % of outages lasting 30 seconds or less, their economic damage can be large. For instance, the impact of power interruptions due to lost time, lost commerce and damage to equipment is estimated at \$75 - \$200 billion per annum in the US [26].

Supercapacitors are better suited to short-term energy storage and are therefore potentially attractive for short-term and high frequency grid stabilisation applications, but they suffer from relatively low energy density of 1 to 30 Wh / kg and up to 10 times higher cost per kWh than Li-ion batteries. Therefore, without major cost changes, supercapacitors are more viable for grid applications where their power rather than energy performance can be appropriately valued, e.g. load levelling and power quality control in smart grids. For these applications, supercapacitors must be able to deliver high power at grid relevant frequencies of 120 Hz down to 1-0.5 Hz, charge / discharge times of 8 ms – 2 s, along with cycle life up to > 10^6 cycles (perhaps up to 15 years) and a round-trip efficiency of > 95 %. Fortunately, supercapacitor maintenance is generally considered to be comparatively easy and low cost, although further improvements will always be desirable.

> Supercapacitors are suited to short-term and high frequency grid stabilisation applications valuing power over energy performance, e.g. load levelling and power quality control in smart grids.

An additional aspect is that, unlike a battery, supercapacitor discharge voltage varies linearly with the charge contained in the system so that additional power electronics are required to ensure a steady output. Although supercapacitors are considered safer than Li-ion batteries, they use similar organic electrolytes to maximise operating voltage (see Equation 5.3) and this presents a possible risk, especially in the event of a packaging leak or facility fire.

For load levelling applications involving a significant penetration of intermittent generating sources (wind and solar), supercapacitors must store and release energy at a moment's notice, easily approaching 10 % of total grid capacity in some instances [27]. In this application, flywheels are generally considered an alternative approach, although supercapacitors generally provide a higher power density of 100,000 W / L compared with ~5000 W / L for flywheels [28, 29]. Specific implementation of grid scale load levelling applications using supercapacitors include a 3 MW, 17.2 kWh and 1 million cycle system to smooth out voltage fluctuations at Yangshan Deep Water Port near Shanghai and

Ireland's Tallaght smart grid test bed that supports a target of 40 % renewable energy generation by 2020.

For industrial sites that have significant local electricity demands, supercapacitors are used for power quality control in the form of uninterrupted power supplies (UPS) to protect critical processing and infrastructure. The worldwide UPS market was estimated at $10 billion in 2016, supporting a growth in smaller, local industrial electricity generation plants using renewable resources. For example, the UPM Caledonian paper mill in Irvine, Scotland was responsible for a third of industrial and commercial regional electricity consumption [30]. A large supercapacitor system was installed in the 1990's to protect some of the most critical processes from voltage dips during adverse weather conditions. The advantage of using supercapacitors instead of conventional electrostatic capacitors was the forecast two orders of magnitude higher energy density that supercapacitors could provide. Most voltage drops, which desynchronise machine drives, take place over 50-150 ms, which can only be partly protected by conventional capacitors, whereas the supercapacitor system is able to protect the plant for 200 ms. More recently, the Caledonian paper mill started to generate electrical and heat energy via biomass using on-site timber resources and supercapacitors were used to store some of the energy generated. By 2010, the 20 MW biomass plant with combined energy storage was capable of providing half of the mill's electricity needs and all of its process steam requirements [31]. Switching to generating and storing energy from biomass also reduced carbon emissions by 75,000 tonnes per annum generated from the site [30].

More recently, the European energy company, ABB, has agreed to supply three state-of-the-art electrical power substations for residential and industrial areas in Dubai in 2016, to address the increasing demand for electricity in Dubai and upgrade the nation's power infrastructure. Each substation will contain supercapacitor banks and power transformers rated at 50 megavolt amperes (MVA) that will improve the stability and quality of power supply during occasional voltage dips. The substations are also planned to be integrated with one of the largest solar parks in the world.

However, most grid storage demonstrators to date simply connect conventional supercapacitors in series to make large assemblies that are not optimised for the grid scale, in terms of safety, cost etc. In the following section, we discuss the research needs for supercapacitors designed for grid-scale storage applications.

> Most grid storage demonstrators to date simply connect conventional supercapacitors in series to make large assemblies that are not optimised for the grid scale, in terms of safety, cost, etc.

5.3. Research needs for grid scale storage

The challenge for further penetration of supercapacitors in grid applications relies on enhancing their energy density, without compromising their defining advantage of high power, reducing cost and ensuring a safe, long and low maintenance working life.

5.3.1. Matching electrode and electrolyte materials

The electrode material typically comprises 40-65 % of the cost of a supercapacitor cell and activated carbon with a high surface area (up to 2,000 m^2 / g) dominates current electrode materials. While carbon particulates continue to show remarkable flexibility in offering variations in surface and internal pore structuring to absorb ions, the highest performing carbons are inherently high cost (e.g. derived from carbides). Graphene may offer ultra-high power performance on account of its very high electrical conductivity, but generally offers only low energy density, unless mounted on relatively expensive substrates. Carbon from bio-derived sources offers the best potential of providing acceptable performance at a lower cost. The key is to develop high surface area bio-derived carbons that minimise costly high temperature processes (such as activation). Significant cost reductions may enable only reasonably performing materials to penetrate grid applications. Aqueous electrolytes and carbon electrodes can offer high power, but the reduction in energy density is generally considered to be unacceptable.

> The key is to develop high surface area bio-derived carbons that minimise costly high temperature processes.

For pseudocapacitors, while notably RuO_2 and MnO_x and some other transition metal oxides have shown high specific capacitance, high energy density and long life in relatively benign aqueous electrolytes, they have not yet shown a clear power-energy-cost-life balance for grid applications. Although they have a reduced electrochemical stability voltage window (Equation 5.2), these systems offer the prospect of better safety and environmental compatibility, as well as lower cost, than organic electrolyte based systems. However, since pseudocapacitative reactions are slower than ion adsorption / desorption behaviour, research efforts are still needed to develop low cost and high performance metal oxide materials that can provide the critical high power capability over long lifetimes. This may be achieved by matching more carefully the surface character of pseudo-capacitive electrode materials to specific aqueous electrolyte ions. To partly mitigate this disadvantage, redox-active electrolytes such as Na_2SO_3 can provide additional capacitance, originating from the reversible redox reactions of the electrolyte itself.

> Research efforts are still needed to develop low cost and high performance metal oxide materials that can provide the critical high power capability over long lifetimes.

An alternative or additional strategy to mitigate the lower operating voltage of aqueous electrolytes is the use of dissimilar anode and cathode materials in asymmetric supercapacitors and, when combined with low cost materials, is likely a key feature of any future grid-relevant supercapacitor. Usually a carbon-based negative electrode is paired with a transition metal oxide-based positive electrode, so that the increased overpotentials at the electrodes delays the evolution of hydrogen and oxygen from decomposition of water, increasing the electrochemical stability window of the system.

For example, Aquion's (US) grid-scale storage technology uses a MnO_2-based cathode, activated carbon anode, cotton-based separator and aqueous Na_2SO_4 electrolyte. Fundamental to materials selection for this arrangement has been the use of relatively cheap, safe and abundant materials. Arising performance may be uncompetitive for traditional supercapacitor applications in mobile systems (per unit weight performance), but is instead targeted for the particular needs of the grid where capital cost ($ / kWh) and lifetime (>10,000 cycles, which determines the period over which capital costs are depreciated) are paramount. Together, an overall performance of 200 $ / kWh is targeted using this approach and evaluation systems at the 1 MWh scale are now being deployed. Similar asymmetric approaches to enhance the energy density performance of supercapacitor-type system have been developed by Saft (France) by pairing nickel oxyhydroxide with carbon for engine start applications and the so-called ultrabattery that uses a hybrid lead-carbon versus lead oxide electrode arrangement to improve the power capability of a lead acid battery. Organic electrolyte (higher voltage) versions of this last approach include an activated carbon electrode paired with $Li_4Ti_5O_{12}$, with attractive power-energy characteristics, but again with scaling challenges for the grid scale.

> The use of relatively cheap, safe and abundant materials is targeted for the particular needs of the grid where capital cost and lifetime are paramount.

While asymmetric arrangements are helping to address the energy density limitations of the otherwise attractive properties of aqueous electrolytes for large systems, the price is almost always a loss of power density, caused by the comparatively sluggish pseudo-capacitive reactions at one or more electrodes. Typically, this pushes the system to applications in the 10 s – several minutes charge / discharge timeframe, whereas responses of < 2 s are needed to access the most valuable frequency regulation applications of grid storage. Therefore, for significant grid applications of supercapacitors, two research paths can be envisaged: (i) aqueous asymmetric systems where low cost, low maintenance and long life are valued sufficiently to compensate for moderate to low energy density and only moderate power density and (ii) symmetric systems where high power is valued sufficiently to compensate for a higher cost (which still needs to be lower than the current cost) and moderate energy density, lifetime and maintenance.

> Two research paths for grid applications of supercapacitors can be envisaged: (i) aqueous asymmetric systems where low cost, low maintenance and long life are valued sufficiently and (ii) symmetric systems where high power is valued sufficiently.

Relatively unexplored further possibilities include the use of ionic liquids as electrolytes with higher operating voltages, but where lower cost and higher ion mobilities are required and solid state devices in which liquid electrolytes replace inherently safe, non-leaking solid state electrolytes but where much higher ion mobilities are needed. Thin film (~1 µm) solid state supercapacitors can offer very high power density, as ion diffusion distances are small, but so far imply enormous and impractical electrode areas in order to provide useful capacities for grid storage.

Up until recently, improving supercapacitor characteristics was seen to be essentially a matter of materials electrochemistry, with manufacturing technology simply an enabling technology to translate promising laboratory systems to larger scale. For supercapacitor electrodes, the manufacturing technology involves casting a slurry of activated carbon, conductive agents and polymeric binder onto a current collector, which is then dried, rolled and assembled into a can or prismatic (pouch) geometry with the electrolyte. Resulting electrodes are typically 50 to 150 µm thick. All promising new material systems for supercapacitors had to "drop in" to this highly productive manufacturing technology. More recently, new manufacturing approaches have been used to better exploit existing chemistries by tailoring the electrode structure to their function more rationally. However, while 3D additive layer, printing and foam based routes have unlocked very high power or energy densities in the laboratory, they are generally unsuitable for the many m^2 of electrode required for grid use. A major research opportunity is the development of manufacturing technologies that approach the productivity of slurry casting, but with an increased degree of micro- and meso-scale control.

> A major research opportunity is the development of productive manufacturing technologies allowing an increased degree of micro- and meso-scale control.

One way to reduce the very large electrode areas implied for grid use is to increase thickness. Freestanding, 2 – 6 mm thick electrodes for grid storage applications have been developed by Aquion using die pressing onto stainless steel foils, followed by packaging into plastic shells. However, care has to be taken to maintain power capability if true supercapacitor (rather than "fast battery") behaviour is required, since otherwise at high cycle frequencies (> a few Hz), progressively more of the electrode area becomes redundant, capacity drops and resistive behaviour develops. Design and simulation tools are required that can optimise the structure of thick electrodes for ionic and electronic conduction, together with new manufacturing technologies that can deliver these designs at an appropriate scale.

6. Redox Flow Batteries

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Redox flow batteries (RFBs) offer the potential to decouple power and energy, making them attractive for higher energy applications. They are commercially available, have demonstrated the ability to operate over large numbers of cycles (>10,000's) and to sustain deep depths of discharge. The current technological challenges involve a requirement for further cost reduction, along with an increase in both power and energy densities. Most of the research challenges lie in the appropriate selection and design of electrodes, electrolytes and membranes to improve current approaches, along with the potential for much lower cost chemistries.

6.1. Introduction to the technology

Redox flow batteries (RFBs) operate by raising / lowering the oxidation state of redox (reduction / oxidation) couples, commonly in liquid electrolytes but sometimes solid or gaseous forms may also be involved. These redox couples are stored in tanks, separate from the power stack, unlike most other secondary battery technologies. The power of the flow battery depends on the size and number of the cells used in the power stack, in which the electrochemical oxidation and reduction reaction occur, while the energy depends on the size of the tanks used to store the produced oxidant and reductant. In charge mode, the cell operates in "electrolyser" mode to regenerate the reduced and oxidised forms of the electrolytes, while in discharge mode the reductant and oxidant are simply flowed back through the power stack, which then works in "fuel cell" mode to produce energy. This allows RFBs to decouple power and energy. The most developed RFB is the all-vanadium system, illustrated schematically in Figure 6.1 and described below.

In discharge mode, vanadium ions in the +2 oxidation state in aqueous solution (anolyte) release electrons at the anode and transform into the +3 oxidation state, as per the following equation:

$$V^{2+}\ (II) \rightarrow V^{3+}\ (III) + e^{-} \qquad \text{(Equation 6.1)}$$

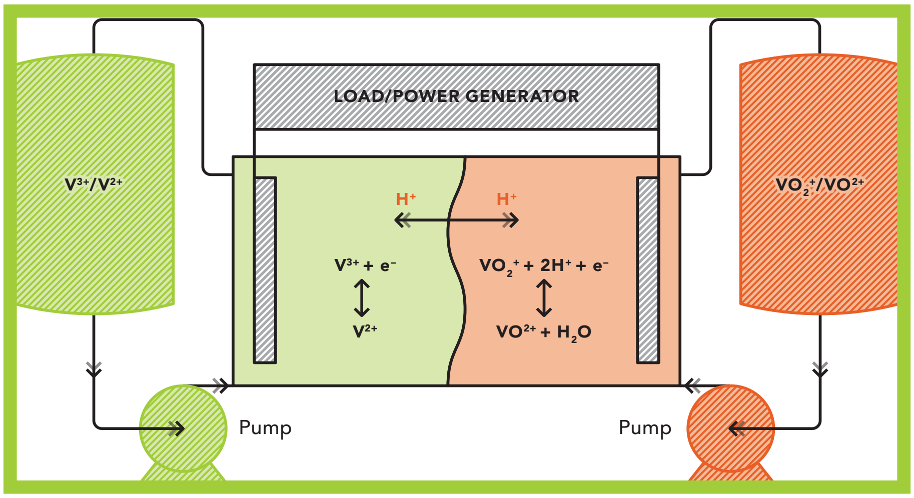
At the cathode, vanadium ions in the +5 oxidation state (VO^{2+}) in aqueous solution (catholyte) receive electrons and transform into the +4 oxidation state (VO_2^{+}) according to:

$$VO_2^{+}\ (V) + 2H^{+} + e^{-} \rightarrow VO^{2+}\ (IV) + H_2O \qquad \text{(Equation 6.2)}$$

The anolyte and catholyte are separated by an ion conducting membrane and are pumped from external reservoirs to the reaction zones at the anode and cathode. In charge mode, the reverse reactions occur, i.e. V^{3+} to V^{2+} and VO_2^{+} to VO^{2+}. The all-vanadium RFB (VRFB) develops an open circuit voltage of 1.26 V per cell, with a typical power density of 0.15 W / cm^2 in the power cell and an energy density of around 50 Wh per litre of solution stored. Round trip efficiency is generally around 75 % at a system level, taking into account electrochemical, shunt current and pumping losses.

FIGURE 6.1

A schematic of an all-vanadium redox flow battery (VRFB) and its operating principles.



6.2. Application to grid scale storage

The two key strengths that VRFBs offer to grid scale storage are:

(i) long lifetimes with a proven capability to operate over >10,000's charge / discharge cycles at deep discharge and >100,000 cycles at shallow discharge;

(ii) the ability to decouple power and energy, offering flexibility for a wide range of applications requiring either high power or high energy.

The range of power and energy best suited to VRFBs and other redox flow systems is tens of kW / kWh to a few MW / MWh. Self-discharge is typically not a problem for VRFB systems, because both electrolytes contain vanadium and can always be recharged back into the initial state. The operational life of a VRFB is determined by a number of factors. The cell stack is probably the most limited life component, with a useful operational life estimated at around 10 years, though capacity loss can also occur over time due to irreversible processes, such as precipitation of the electrolyte constituents.

> VRFBs offer two key strengths to grid scale storage: long lifetimes and the decoupling of power and energy.

VRFB systems are rated at many 10,000's cycles with no limits of depth of discharge (DOD). For example, a 4 MW / 6 MWh VRFB plant installed in Japan in 2005 (Prudent Energy) can withstand a temporary overload of up to 6 MW and is intended for smoothing power output fluctuations at Subaru Wind Villa Power Plant, rated at 30.6 MW. The system consists of 4 banks, each made of 24 stacks and rated at 1 MW (maximum 1.5 MW). Each stack consists of 108 cells, with a rated power of 45 kW. With over 3 years of operation, it completed more than 270,000 cycles successfully [32], though these are likely to be shallow rather than deep levels of discharge.

A key challenge for VRFBs is the relatively high cost of the technology at present, reflecting the cost of the vanadium electrolyte, the power cell and the auxiliary plant. Pacific Northwest National Laboratory (PNNL) has published a useful model to assess RFB costs [33]. The model estimates near-term costs for a VRFB system at around 4,000 $ / kWh for a 1 MW / 0.25 MWh system and around 475 $ / kWh for a 1 MW / 4 MWh system, showing the sensitivity of cost to energy requirements. In the latter case, the dominant contributors to the costs of the system are the vanadium electrolyte (43 %) and the membrane in the power cell (27 %). Examples of developers of this technology include Prudent Energy, UniEnergy Technologies, Gildemeister Energy Solutions, and the UK company, RedT.

> The dominant contributors to the costs of the system are the vanadium electrolyte and the membrane in the power cell.

One of the reasons for the cost of the technology is the relatively low power density achieved in the power stack, meaning that large amounts of high cost ion exchange membranes are required, as well as other cell materials. For example, a typical VRFB currently operates at a power density of around 0.15 W / cm^2. This is approximately only 10 % of the power density achieved in low temperature fuel cells, which are based on similar ion exchange membranes. Recent work in the USA has shown that this can be improved in a VRFB to around 1 W / cm^2 by optimising the mass transport within the cell [34]. Whilst it is unrealistic to expect all this performance gain to be realised at larger scale, it nonetheless shows the potential for cost and size reduction.

A further challenge for VRFBs is the relatively low energy density of the electrolyte. The solubility of vanadium in the +5 oxidation state is around 2 mol / L, depending upon temperature and electrolyte composition. This translates into an energy density of around 50 Wh / L, meaning that to attain an energy output of 1 MWh, the system requires 20 m^3 of each solution, i.e. tanks with around 2 m diameter and 6 m height. These volumes could be reduced if the solubility of vanadium containing electrolytes can be increased.

The relatively high cost of vanadium is driving the development of alternative RFB chemistries and there has been a surge of interest in new chemistries in the past ten years, aimed at lowering cost and/or increasing energy density [35]. Despite this, currently only two other RFB technologies have reached a level of technological and commercial maturity: Fe/Cr (e.g. Deeya Energy, EnerVault) and Zn/Br (e.g. ZBB Power, RedFlow).

> There has been a surge of interest in new chemistries, aimed at lowering cost and/or increasing energy density.

Zn/Br is a hybrid RFB, because it is based on the electrodeposition (charge) and electrodissolution (discharge) of metallic zinc on the anode and the bromine/bromide redox couple at the cathode. As a result, energy and power are not totally decoupled, as the metallic zinc is located within the power conversion cell. Having a theoretical OCP of 1.83 V per cell, the Zn/Br system utilises a relatively cheap $ZnBr_2$ electrolyte for both the anolyte and catholyte compartments. During charge, zinc is electrodeposited on the anode and bromine is produced at the cathode, forming a polybromide complex. The presence of a highly corrosive and toxic bromine means that there are chances of corrosion of cell components on one side, while zinc dendrites on the other side result in non-recoverable capacity loss and self-discharge.

The Iron-Chromium RFB has a theoretical OCP of 1.1 V per cell and uses two liquid electrolytes. A key driver for this chemistry is the use of much lower cost electrolytes than the all vanadium case, but with the challenge that it is susceptible to non-recoverable crossover of the redox couples across the membrane and sluggish Cr redox kinetics, reducing cycle life and performance.

6.3. Research needs for grid scale storage

In order to make RFBs attractive for grid storage applications, key challenges in two main areas of research and development should be addressed: substantial cost reduction of the RFB systems and considerable improvement in power and energy density.

6.3.1. Cost reductions in electrolytes

Commercially available RFB systems utilise relatively costly electrolytes based on vanadium, chromium or bromine-organic complexants. They may be replaced by significantly cheaper materials. Though some initial work has already been carried out, there remains a very large field of research into stable, highly soluble and reversible redox couples. Another approach is to use air for the cathode redox reactions, resulting in a lower cost liquid-air flow battery. A specific example of such an approach is the zinc-air flow batteries that are under development. However the use of air based flow batteries requires significant improvement in the performance and long-term stability of the electro-catalysts used within the air electrode.

6.3.2. Cost reductions in membranes

Nafion membranes have demonstrated high levels of performance and lifetime in both fuel cell and redox flow battery applications. However, their cost is high and is not expected to drop appreciably. Novel types of durable and highly conductive ion-exchange membranes with low cost production are required. These new membranes do not need to be as universally applicable as Nafion, but instead could be tailored for specific chemistries. Both acidic and alkaline membranes should be considered to open up a greater range of potential flow battery chemistries. Mechanical and chemical stability in the environment are important and need to be maintained over 10,000’s cycles. The membranes need to inhibit the crossover of active components.

> Novel types of durable and highly conductive ion-exchange membranes with low cost production are required.

6.3.3. Cost reductions in flow cell components

Many flow batteries use relatively costly graphite to manufacture flow distribution and interconnect plates. Research is needed to develop lower cost alternatives, such as composite conductive plastics that will be stable in corrosive environments, have a sufficiently high electronic conductivity to minimise Ohmic losses and can be manufactured in the large areas needed within flow batteries.

6.3.4. Improved performance and operational life: porous electrodes

The active surface of electronically conductive carbon felts and papers commonly provide the sites for the electrochemical redox reactions. Novel synthesis routes to increase the effective active area per unit, with cost-effective post processing treatments like oxidation / coating for surface modification, need to be developed to fabricate mechanically stable and corrosion resistant porous media, of both carbon and/or other materials depending on the cell chemistry. There are two main flow configurations used in redox flow cells - one using a flow-through approach in which the electrolyte passes through the porous electrode, the other one utilising a flow-by design in which transport into the electrode relies on diffusion. The former employs relatively thick carbon felts (a few mm in thickness) while the latter uses a much thinner carbon paper. Flow battery power density is currently limited by mass transfer in these electrodes. Hence both configurations need improvement through optimisation of fluid flow within the structure, whilst maintaining good electronic conductivity and electrochemical activity. This could be accomplished through the design and manufacture of optimum porous 3D structures via advanced 3D characterisation, high fidelity modelling and simulation, as well as the design and manufacture of high performance electrodes, for example by utilising additive manufacture coupled with other processes.

> Optimisation of fluid flow within electrodes could be accomplished through the design and manufacture of optimum porous 3D structures, for example by utilising additive manufacture.

In addition to enhancing mass transfer rates, which is a key requirement for vanadium flow batteries, other newer chemistries will continue to need improvement to, and development of, electrocatalysts to reduce overpotential losses and/or unwanted side reactions (such as hydrogen evolution) and hence improve round trip efficiency.

6.3.5. Improved performance and operational life: auxiliary components

Sometimes overlooked, the auxiliary components can play a significant role in extending the life of the system. Bespoke control algorithms should be tailored to a specific chemistry and system used and be equipped with a fast yet reliable embedded model that takes note of degradation effects and state of health, adjusting operation of ancillary systems accordingly. Lower cost power conditioning systems are required and auxiliary components such as pumps need to be tailored for these applications, to reduce cost and enhance lifetime.

7. Compressed Air Energy Storage

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The most commonly used grid scale energy storage technology at present is Pumped Hydro Storage (PHS). However, potential sites within the UK for future PHS systems are very limited. Compressed Air Energy Storage (CAES) has the second largest storage capacity and has been in use as a peak shaving option since the 1970s. CAES has significant potential – with low costs (both initial investment and recurrent), low pollution potential, long life and suitability to work well at both large (>100 MW) and small scales (<1 kW). It is known that the UK potential salt deposit can create salt caverns with over 1,000 GWh of compressed air energy storage capacity. CAES could be one of

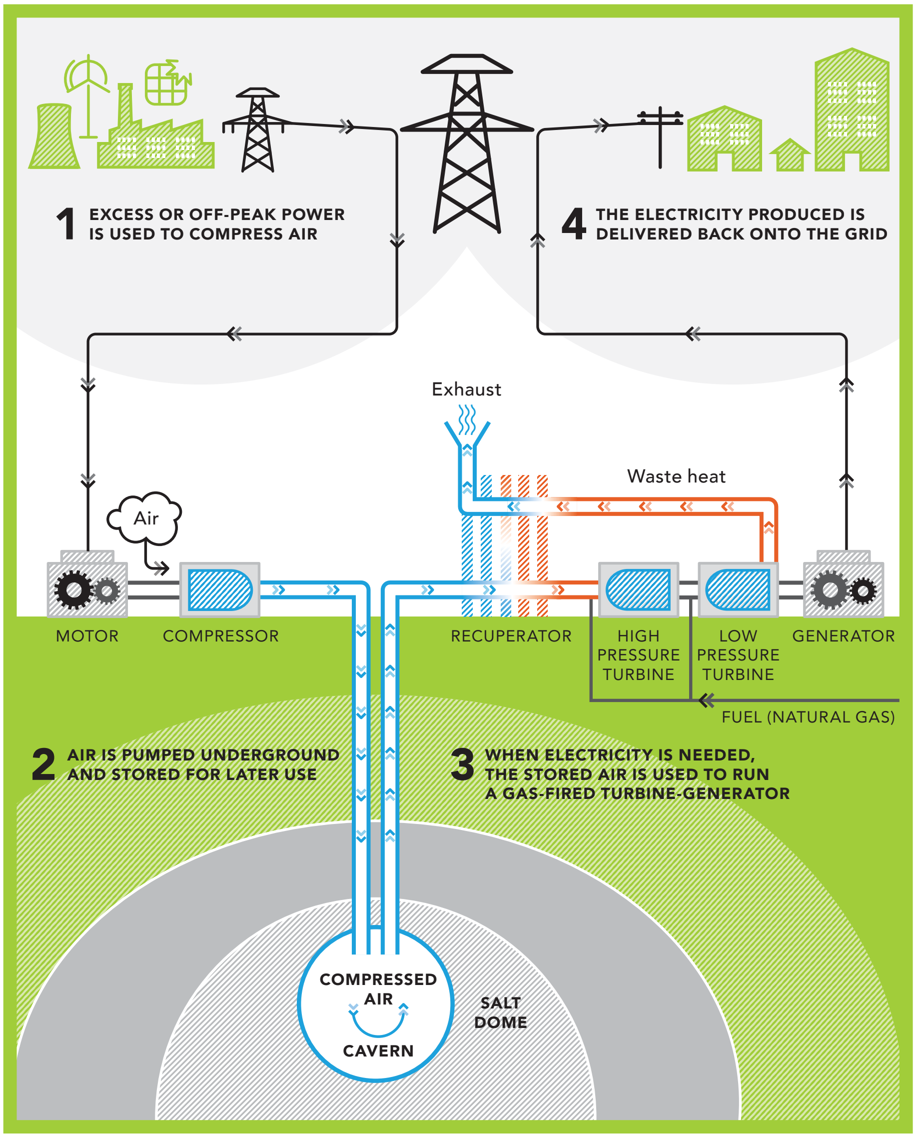


FIGURE 7.1
Schematic diagram of a compressed air energy storage (CAES) system [36].

the storage technologies that fits for the UK and is appropriate for deployment at both the large scale for grid connections and the small scale for distributed energy storage.

7.1. Introduction to the technology

CAES refers to a process of storing energy in the form of high pressure, compressed air during the periods of low electric energy demand and then releasing the stored energy for electricity generation during peak demand [37]. A typical conventional large-scale CAES plant is shown in Figure 7.1, from which it can be seen that a CAES system includes air compression, storage (into underground caverns or over-ground tanks), expansion with gas turbines and electricity generation. The generator / motor unit is linked with all compressors and turbines through a common shaft. A clutch mechanism decides the practical performance of the plant and the operation sequence. The world's first utility-scale CAES plant was installed and commissioned to operation by Asea Brown Boveri (ABB) in Huntorf, Germany, in 1978 [38]. It has a rated power of 290 MW, providing load following services and meeting the peak demand while maintaining constant capacity factor in the nuclear power industry [38, 39]. In 1991, another large-scale CAES plant commenced operation in McIntosh, Alabama, US [39]. The 110 MW plant, with a storage capacity of 2,700 MWh, is capable of continuously delivering its full power output for up to 26 hours.

A recent development in CAES is to avoid using additional fossil fuel via an Adiabatic CAES (A-CAES) process, illustrated in Figure 7.2. Air is adiabatically compressed and pumped into a storage reservoir and the heat generated through air compression is stored. When the A-CAES system is operated in its expansion mode, the compressed air recovers the stored thermal energy and passes it through an air turbine for power generation. In addition, small scale CAES systems are also under development. Energetix Group (now Flow Group) launched its small-scale compressed air Uninterrupted Power Supply (UPS) products to the market [40] in 2009. Also, Liquid Air Energy Storage (LAES) can be considered as a variant of CAES, since many important components needed to build a LAES system are also required by CAES, such as compressors, turbines /

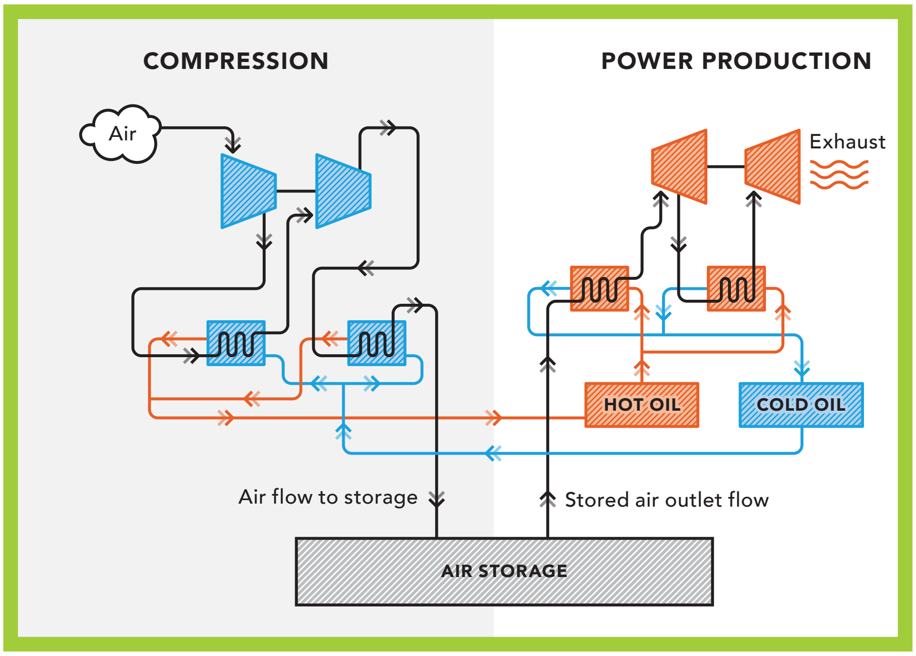


FIGURE 7.2
Schematic layout of an Adiabatic Compressed Air Energy Storage (A-CAES) plant [42].

expanders, electric motors / generators and sometimes heat exchangers. The UK based Highview Power Storage implemented a pilot LAES facility (300 kW /2.5 MWh storage capacity) [41] and this is discussed further in the section on thermal energy storage.

7.2. Application to grid scale storage

CAES facilities can be built to various scales, from a few kW to over 1,000 MW [40, 43]. Thus large scale CAES can be used for grid-scale energy management in supporting load shifting, peak shaving and load levelling. The smaller scale CAES can be used as an alternative to replace traditional chemical batteries and mechanical flywheels in back-up power and UPS applications. With moderate response speeds and good partial load operations, CAES offers strong potential for integration with intermittent renewable energy power generation in either distributed or centralised modes. Table 7.1 identifies potential application areas for CAES.

> With moderate response speeds and good partial load operations, CAES offers strong potential for integration with intermittent renewable energy power generation in either distributed or centralised modes, but low energy storage density is one of its major weaknesses.

7.2.1. CAES potential in the UK

It is well known that low energy storage density is one of the major weaknesses of CAES. Although the cost of CAES is comparable to PHS [37], the development and deployment of large scale CAES relies on natural geological conditions to provide large reservoir volumes. Fortunately, the UK has good salt deposits, offering the natural conditions for making salt caverns, so the UK is relatively rich in underground natural resources, as illustrated in Fig. 7.3. The process for creating salt caverns is less complicated than constructing rock caverns, meaning that the cost for making salt caverns is around 50 % of the cost for building rock caverns, per cubic meter. From the study conducted by the British Geological Survey [44], the total volume of the currently existing salt caverns used for natural gas storage in the UK is around 13,000,000 m^3, capable of storing over 100 GWh energy in the form of compressed air at 80 bar storage pressure. This volume of storage capacity is actually only a small percentage of the UK total available storage capacity. The estimated capacity in the UK for CAES could be higher than 1,000 GWh, based on the study conducted by the IMAGES project [45].

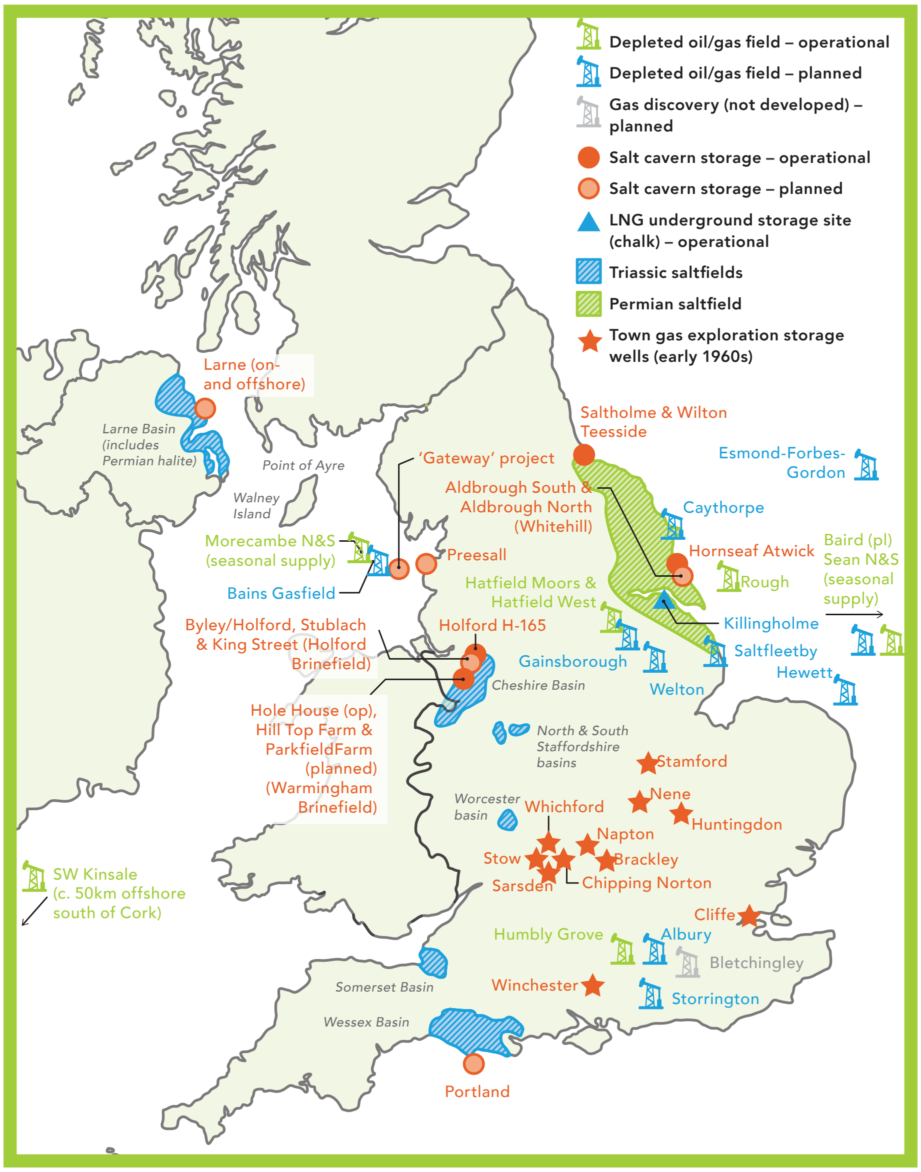
> The UK is relatively rich in underground natural resources. The estimated capacity in the UK for CAES could be higher than 1,000 GWh.

7.3. Research needs for grid scale storage

7.3.1. Formation of Salt Caverns

Salt caverns for compressed air storage can be developed through solution mining techniques, providing a low cost and reliable approach. Solution mining is a technique using water or other liquids to dissolve and extract salt from salt strata, thereby forming a large cavity in the salt with the appropriate size and shape. The elasto-plastic property of salt means that the cavern walls retain their structural integrity even after successive pressurisation cycles, thus salt caverns can make good reservoirs to suffer minimal degradation in long term usage and pose minimal risks of air leaks [46, 47]. To make the process economic, the process should maximise the size / volume of the caverns for each salt mining well drill. Also, the shapes of caverns will affect the size of their volume and also result in different impacts on the cavern structure when the pressure changes during charging / discharging. Research is required into site characterisation and the optimal forms of storage caverns to enable high efficiency operation. Costs related to the location of the energy source relative to the storage site(s) need to be examined in techno-economic analyses.

FIGURE 7.3
Locations of operational and proposed UK underground gas storage sites [44].



Application area	Characteristics			Suitable or potential CAES related technology
	Capacity	Response time	Discharge duration	
Power quality	~<1 MW	~ms, <1/4 cycle	ms to s	Hybrid systems with small-scale CAES and battery or supercapacitor or other EES technologies with fast response.
Energy management	Large-scale (>100 MW); medium/small-scale (<100 MW)	minutes	up to days	Large-scale energy management (large-scale CAES); Small-scale energy management (small-scale CAES, LAES).
Renewable back-up power	~100 kW - 40 MW	s to minutes	up to days	Multi-scale CAES, hybrid systems with CAES and capacitor or others with fast response may need, possible LAES.
Emergency back-up power	Up to ~1 MW	ms to minutes	up to ~24 hours	Possible small-scale CAES, hybrid systems with small-scale CAES and other technologies with fast response.
Time shifting	~1 MW - 100 MW and even more	minutes	~3-12 hours	Multi-scale CAES and LAES.
Peak shaving	~100 kW -100 MW and even more	minutes	hour level, ~<10 hours	Multi-scale CAES and LAES.
Load levelling	Up to several hundreds of MW	minutes	up to ~12 hours and even more	Multi-scale CAES, possible LAES.
Seasonal energy storage	~30 MW - 500 MW	minutes	weeks	Possible large-scale CAES and LAES.
Black-start	Up to ~40 MW	minutes	s to hours	Multi-scale CAES, possible LAES.
Spinning reserve	Up to MW level	normally up to a few s	30 minutes to a few hours	Possible the hybrid system with small-scale CAES and capacitor or other EES technologies with fast response.
Uninterruptible power supply	Up to ~5 MW	normally up to s	~10 minutes to 2 hours	Hybrid system with small-scale CAES and supercapacitor or other EES technologies with fast response, e.g. Pnu power.
Standing reserve	Around 1-100 MW	<10 minutes	~1-5 hours (storage time at rated capacity)	Promising multi-scale CAES and LAES.
Transmission upgrade deferral	~10 - 100+ MW	~minutes	1-6 hours (storage time at rated capacity)	Promising multi-scale CAES and LAES.

TABLE 7.1
Potential applications of CAES related technology [37].

> Research is required into site characterisation and the optimal forms of storage caverns to enable high efficiency operation.

7.3.2. Improvement of round trip efficiency

One of major barriers for acceptance of CAES is its low round trip efficiency. The Huntorf plant has a cycle efficiency of 42 % and the cycle efficiency of the McIntosh plant is about 53-54 % [39, 43]. The low efficiencies of CAES result from the heat losses in the compression and expansion modes, air leakage throughout the whole CAES system and internal energy losses due to the air compressibility. A-CAES combined with adequate thermal energy storage will reduce heat losses and is expected to achieve 70 % cycle efficiency. To improve CAES round trip efficiency, the following research is required: i) suitable thermal storage procedures and facility design to maximise the utilisation of thermal energy stored, such as high pressure thermal storage; ii) whole system efficiency analysis, system optimal design, optimal coordinate control and operation optimisation are needed, since the individual components or devices working at their optimal status does not mean that the whole system is in its optimal status, due to complicated coupling effects. The key technology challenges are presented in efficient utilisation of thermal energy released from the compression process.

7.3.3. Innovation in turbo machinery design and manufacturing technology

The UK company, Flowbattery, is a good example of the importance of technology innovation. By adopting an innovative scroll air expander technology, the company developed its product, the Compressed Air Battery, achieving an air-to-electricity conversion efficiency of around 90 %. Technical innovations and technology breakthroughs are essential, especially for high pressure compressor and turbine technology, such as developing improved sealing methods for compression and expansion machinery to suppress internal leakage and discovering approaches to minimise losses associated with secondary flows in compressors and turbines. Research on innovative technologies is the key for realisation of the potential of CAES.

> The key challenges are presented in efficient utilisation of thermal energy released from the compression process and innovations in compressor and turbine technology.

7.3.4. Innovation in small scale CAES systems (<10 MW)

In general, the larger the scale of CAES, the more efficient the system. However, this perception is changing. Small scale CAES units have started to demonstrate their value in recent years when used to replace chemical batteries in some applications. Also, small scale CAES can be used in distributed energy storage to serve distributed power generation. In addition to research efforts on large scale CAES, it is essential to make efforts on small scale CAES research. The progress of small scale CAES depends on the development of new and innovative technologies.

> Small scale CAES can provide distributed energy storage to serve distributed power generation.

7.3.5. Integrated technologies

CAES on its own has relatively low round trip efficiency. Integrated utilisation of energy through the whole process can increase the round trip efficiency, as the energy losses can be recovered via the integrated process. Integration should focus on: i) integration of CAES with wind / solar power generation, storing energy locally and maximising the renewable power generation [48]; ii) integration of CAES with heating and cooling systems, in which the heat from compression and the heat losses from expansion can be used directly, for example, a compressed air battery installed in a data centre with the cool air from the exhaust being circulated around the centre for cooling [37]; iii) integration with thermal storage to maximise its compression efficiency and iv) integration with other energy storage technologies, to operate at its most efficient range.

> Integration of CAES with renewable power generation systems, heating / cooling systems and other energy storage technologies can increase round trip efficiency through integrated utilisation of energy in whole processes.

8. Thermal Energy Storage

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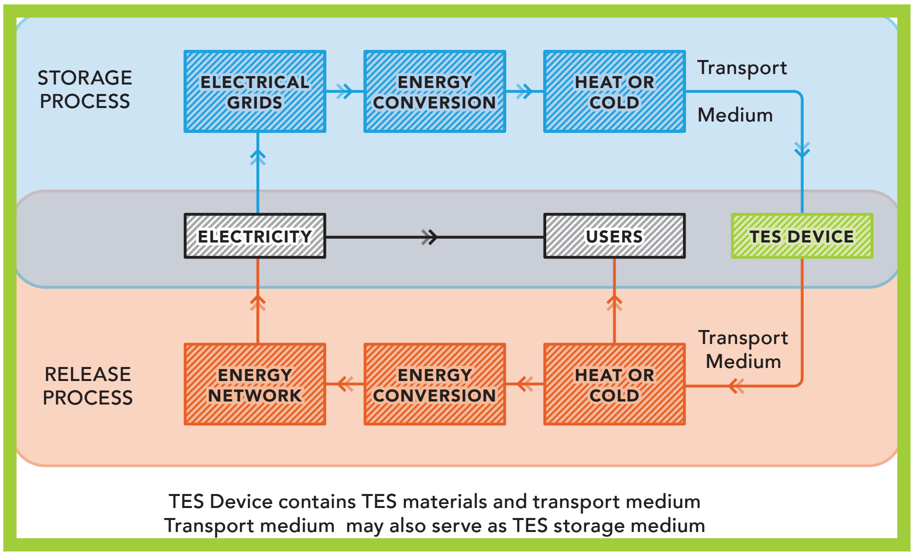
Thermal energy storage (TES) refers to a collection of technologies that store energy in the forms of heat, cold or their combination, currently accounting for approximately 55 % of global non-pumped hydro installations. The main grid scale TES technologies include cryogenic energy storage (CES) [49], heat energy storage (HES) [50, 51] and pumped thermal electricity storage (PTES) [52]. Current TES technologies have a response time of approximately two to a few tens of minutes and are therefore mainly for energy, rather than power applications in electrical grids. Key research needs for TES include: (i) novel materials, components and devices for enhancing response time; (ii) low cost manufacturing technologies for TES materials, components and devices; (iii) degradation mechanisms of TES materials; (iv) novel thermodynamic cycles for enhancing conversion efficiency and (v) integration and optimisation of TES in electrical grids.

FIGURE 8.1
The concept of thermal energy storage (TES).



8.1. Introduction to the technology

Grid-scale TES refers to a collection of technologies that store energy in thermal forms (heat and/or cold) and use the stored thermal energy either directly or indirectly through energy conversion processes when needed. Fig. 8.1 illustrates the concept, assuming the input and output energy forms are electricity; similar diagrams can be obtained from other energy forms. TES is usually classified into three categories: sensible heat storage (SHS), based on temperature difference, latent heat storage, based on the so-called phase change materials and thermochemical energy storage (TCES), based on adsorption / desorption, absorption / desorbtion, or reversible chemical reactions. TES currently accounts for approximately 55 % of global non-pumped hydro installations.

The main grid scale TES technologies under development include CES, HES and PTES. These technologies rely on both the SHS and LHS principles. For grid scale applications, CES and HES usually store high grade cold (<-100 °C) and high grade heat (>300 °C) respectively, whereas PTES stores both heat and cold and can therefore be regarded as a combination of CES and HES.

8.2. Application to grid scale storage

Grid scale TES technologies can be used as a standalone system for energy applications; they can also be used in combination with other energy storage technologies for both energy and power applications. TES is essential for Adiabatic Compressed Air Energy Storage (A-CAES) for round trip efficiency enhancement (see Section 7) and solar thermal power generation for dealing with intermittency. The most significant and perhaps unique aspect of TES lies in the benefits of enhanced overall system efficiency, reduced cost in carbon capture and increased peak shaving capacity, upon integration of the technology with energy networks.

> TES enhances overall system efficiency, reduces cost in carbon capture and increases peak shaving capacity, when integrated with energy networks.

8.2.1. Cryogenic Energy Storage (CES)

CES can use different storage media, including air, nitrogen, natural gas, or even some organic liquids, etc. The most developed CES technology uses nitrogen, storing high grade cold in liquid nitrogen at the extremely low temperature of -196 °C. The following discussion will focus on liquid nitrogen / air based CES - so-called liquid air energy storage (LAES).

FIGURE 8.2
LAES pilot plant (350 kW / 2.5 MWh) at the University of Birmingham campus.

Advantages and disadvantages: LAES has a volumetric exergy density exceeding 660 MJ / m^3, considerably higher than CAES (~60 MJ / m^3 at 100 atm storage pressure). It can use existing infrastructure for the air liquefaction and gas sectors. The technology has no geographical constraints and does not need the use of any exotic materials. LAES has a relatively long storage duration (hours to weeks) and a relatively short response time (~2.5 min is achievable) [53]. It has a high cycling ability with an expected life span over 20-40 years and minimal degradation in terms of depth-of-discharge. Another advantage unique to LAES is due to the very low critical temperature of air / nitrogen compared with steam and many other working fluids, enabling highly efficient waste heat recovery through integration (~4 times more efficient than Organic Rankine Cycles) [54]. However, an independent LAES system (without external waste heat source) has a relatively modest round-trip efficiency of below ~60 % [55]. Full LAES systems only work economically at large scales (tens of MWs) using current liquefaction technology, though the power recovery part of an LAES system could also work economically at small and medium scales, should efficient expanders be available [56]. For a 50 MW / 200 MWh unit, the cost is forecast to be ~1,000 £ / kW and ~250 £ / kWh.

> LAES offers high energy density, long storage duration, short response time and long lifespan. It can use existing infrastructure, has no geographical constraints and uses no exotic materials.

Current state-of-the-art: The UK is internationally leading in research and development. On the commercial front, CES is currently at the pre-commercial stage. A 350 kW / 2.5 MWh full pilot plant, now on the University of Birmingham Campus (Figure 8.2), has been built by Highview Power Storage Ltd, a UK-based company. This has demonstrated the feasibility of the technology and the company is currently building a larger scale plant rated at 5 MW / 15 MWh. A number of other companies, including Hitachi, Mitsubishi and Air Products, have also done some work on CES, but their work has not led to any fully integrated plant so far.

8.2.2. Heat Energy Storage (HES)

HES includes SHS, LHS and TCES, with SHS storing heat in solids and liquids, LHS through solid-solid and liquid-solid phase change and HES in the form of adsorption / absorption / reaction enthalpy change due to interactions among liquid, solid and gas molecules. For grid scale applications, high energy densities and acceptable round trip efficiencies usually require SHS storing heat at temperatures over ~300-500 °C, LHS using phase change materials with phase change temperature over ~300-500 °C and adsorption / absorption / chemical reactions of TCES systems taking place at ~300-500 °C.

Advantages and disadvantages: Overall, HES technology is the cheapest among all energy storage technologies. Within the HES technology family, SHS is the cheapest (can be <5 £ / kWh), followed by LHS (generally <50 £ / kWh) and TCES is the most expensive (>100 £ / kWh). SHS has a low energy density (tens to a few hundreds of kJ / kg) and hence is very bulky; LHS has a much higher energy density (hundreds to over a thousand kJ / kg); TCES could have the highest energy density among all energy storage technologies. SHS and LHS can store energy for hours to days, whereas TCES can have a long storage duration from months to years. HES has a response time of several to tens of minutes and is therefore mainly for energy rather than power applications.

> Heat Energy Storage, particularly Solid Heat Storage, is the cheapest among all energy storage technologies. The response time of HES makes it best suited to energy rather than power applications.

Current state-of-the-art: In the HES family of technologies, SHS is well developed and has been widely used in various industrial sectors; LHS is less developed with a limited number of applications; TCES is least developed and has little application so far. Currently, only SHS has been used for grid scale applications. Examples include: (i) concentrated solar power (CSP) plants where thermal oil (e.g. Therminol VP-1) and nitrate based molten salt (solar salt) are used as the materials for SHS and the oil and molten salt are also used as heat transfer fluids [57]; (ii) conventional power plants, where steam is stored in steam accumulators for peak shaving and (iii) electrification of heat, where hot water is produced and stored in large tanks at off-peak hours and used at peak hours for space heating. Currently, Germany, Spain and the USA are internationally leading in HES research and development. Germany (DLR) has established a 750 kWh demonstration unit using both SHS and LHS, having a power rating of 1 MW. The UK is leading in LHS materials research, particularly in formulation, characterisation and manufacture of high temperature composite LHS materials (Fig. 8.3).

FIGURE 8.3
LHS materials formulation, using the meso-scale engineering method.

8.2.3. Pumped Thermal Electricity Storage (PTES)

PTES can be regarded as a combination of CES and HES, in terms of storage, and the main difference lies in the use of heat pump / heat engine mechanisms in the energy conversion steps [58].

Advantages and disadvantages: The PTES process is based on well-established heat pump and heat engine mechanisms coupled with heat and cold storage. For grid scale applications, the technology requires storage of both heat and cold at high grade for an acceptable level of energy density and round-trip efficiency. As a result, PTES should have features similar to that of the CES and HES technologies – no specific geographical locations, little environmental impact, favourable volumetric energy density and a focus on energy rather than power applications in electrical grids. The main challenges associated with PTES lie in sufficiently reducing the exergy losses to obtain a good round trip efficiency. This is because a complete charge and discharge cycle involves twice as many compression, expansion and heat transfer processes, each resulting in a degree of irreversibility. The compressor-expander coupled machinery transfers a portion of the incoming and outgoing work into additional heat. In order to decrease the efficiency loss in this process, high isentropic efficiency of the machinery is required in both forward spin and reverse spin. Additionally, new compression / expansion machinery must be developed for the specific working fluid (e.g. the monatomic gas).

> For grid scale applications, Pumped Thermal Electricity Storage requires storage of both heat and cold at high grade for an acceptable level of energy density and round-trip efficiency.

Current state-of-the-art: PTES technology is at the stage of validation through whole system demonstration at both lab and pilot scales. A UK based company, Isentropic, was developing the technology, but went into administration in January 2016. At the heart of their design is a reversible reciprocating heat-pump / heat-engine allowing the grid to respond to variation in load and generation. Isentropic expects that with argon as the working fluid, maintaining a topping pressure of 12.13 bar and hot and cold storage temperatures of 500 °C and -166 °C respectively, a round-trip efficiency of 72 % could be achieved. In 2012, Isentropic announced a $22 million investment from the UK government-backed Energy Technologies Institute (ETI), with a short-term goal of deploying a 1.5 MW / 6 MWh system at a levelised cost of storage of 35 $ / MWh. A number of other companies, including Alstom, GE, ABB and Saipem, have also done some work in this area. However, a fully integrated system is yet to be demonstrated.

8.3. Research needs for grid scale storage

TES can be classified into SHS, LHS and TCES, according to physical principles [43]. They are at different development stages and have some common and also some very different characteristics. As a result, there are different research needs for the three categories of TES technologies. An attempt is made in the following to summarise both the common and different research needs for the three grid scale TES technologies, in order to make them commercially competitive.

Fundamentally, across all TES technologies, there is a need to understand the relationships between properties and behaviour of TES materials, components, devices and systems, as illustrated in Fig. 8.4, as well as how the manufacturing processes of the materials, components and devices affect these relationships. This is a multidisciplinary problem, involving a wide range of length scales, from ~10^{-10} – 10^{3} m. More specifically, the research challenges associated with grid scale TES technologies include the following areas.

> Understanding relationships between properties and behaviour of TES materials, components, devices and systems is key to its success. This is a multidisciplinary problem, involving a wide range of length scales.

TES materials for LHS and TCES technologies: Novel materials are needed to increase further energy and power densities, in order to achieve a reduced footprint, rapid response time and reduced cost of the TES technologies [59]. This line of research also needs to address challenges associated with: (i) mechanical degradation due to volume change induced structural failure resulting from phase change, adsorption / desorption, or reversible reactions during cyclic operations; (ii) chemical degradation due to interfacial corrosion,and contamination from trace components in heat transfer fluids, encapsulating materials, or reactants during the cyclic operations; and (iii) rapid screening and testing methods for TES materials.

> Research challenges include understanding mechanical and chemical degradation of TES materials and development of rapid screening and testing methods.

TES components and devices for SHS, LHS and TCES: Most conventional TES components and devices are based on packed beds, fluidised beds, or two-tank units. These configurations often give either a slow response (packed beds and two-tank units) or degradation of thermal energy grade (fluidised beds). The degradation of thermal energy grade implies high exergy losses and hence low round-trip efficiency. Novel designs are needed to address these issues. This line of research also needs to address: (i) scale-up of TES components and devices for which little has been done and (ii) development of novel thermodynamic processes and cycles for reducing heat and mass transfer resistance, while improving electricity-thermal energy conversion efficiency.

> Novel designs of TES components and devices are needed to improve round-trip efficiency.

Integration of TES technologies in electrical grids: Unique to TES technologies are the potential benefits of enhanced system level efficiency, reduced costs and increased peak shaving capabilities. To achieve these potentially additional benefits, integration and optimisation of TES into the energy network is essential, particularly under dynamic conditions [56, 60, 61]. A specific challenge to this lies in the development of simple algorithms that capture the most important features to enable the rapid computing and process control needed for electrical grids.

Low cost manufacturing technologies for LHS and TCES: Manufacture of TES materials, components and devices for LHS and TCES with consistently high quality at low cost can be highly challenging. Little research has been done in the area.

FIGURE 8.4
Identification of research needs for grid scale TES.

9. Power to Gas

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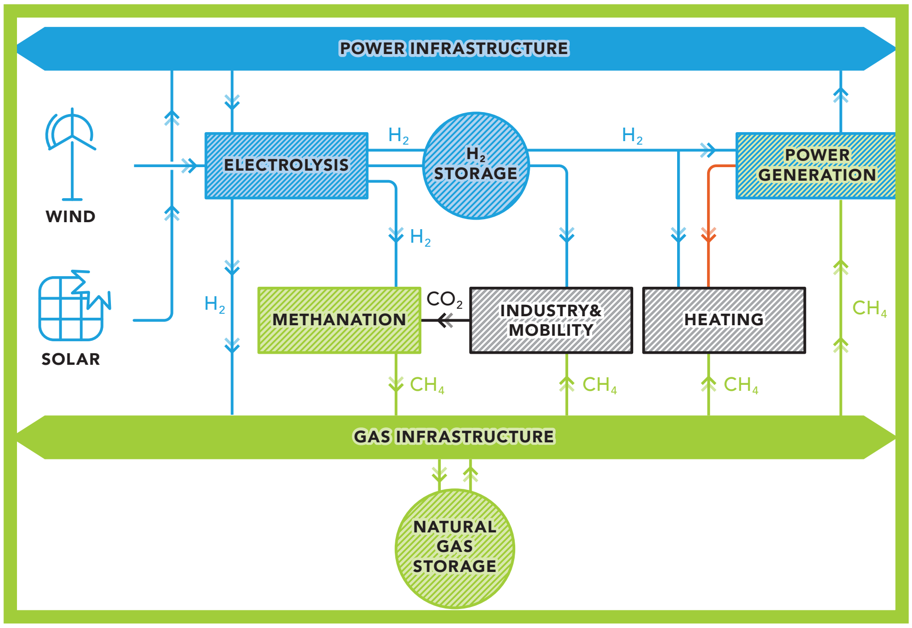
Power to Gas (P2G) is a concept in which electricity is converted into chemical energy, in particular hydrogen and/or synthetic methane, and then either this gas is used directly, for example as a transport fuel in the case of hydrogen, is converted back into electricity in a fuel cell or gas turbine, or it is injected into the gas network. P2G not only offers energy storage potential, but it could also help decarbonise other sectors, such as heat and the industrial sector. The current technological challenges involve a requirement for further cost reduction and round trip efficiency improvement, along with flexible operation to accommodate variable power input.

FIGURE 9.1
Illustration of the Power to Gas (P2G) Concept [62].



9.1. Introduction to the technology

P2G always involves the use of electrolysis to convert electrical energy into chemical energy, in the form of hydrogen. Interest is also emerging in the potential to use high temperature electrolysis to convert a mixture of steam and carbon dioxide directly into syngas (the building block of many other chemicals, for example, methanol). There is also interest emerging in the potential to combine electrolytically produced hydrogen with captured carbon dioxide in a methanation reactor (either thermochemical or biological) to produce synthetic methane. Figure 9.1 illustrates the concepts.

Electrolysis requires high water purity. Therefore, a treatment step is required in which minerals and ions are removed prior to electrolysis. After de-ionisation and demineralisation, the water is split into hydrogen and oxygen by applying a direct electric current in an electrolyser to drive the water splitting reaction:

$H_2O(l)$ -> $H_2(g) + 0.5O_2(g)$ (Equation 9.1)

There are three main types of electrolyser available. Alkaline water electrolysers have been commercially available for many years, proton exchange membrane electrolysers are becoming commercially established and solid oxide electrolysers (which, in principal, offer the lowest electrical energy consumption) are under development.

If the hydrogen is to be combined with carbon dioxide to make synthetic methane, then this can be done in the thermochemical Sabatier process, in which the overall reaction is exothermic, as shown below:

$CO_2(g) + 4H_2(g)$ (arrows) $CH_4(g) + 2H_2O(l)$ ($\Delta H = -165$ kJ / mol) (Equation 9.2)

This process is well established, operates at large scale (>10's MW) and operates with an efficiency of 70-85 % depending on the conditions used, with the balance of energy emitted as heat. Emerging alternatives to this are biological processes, which can operate at smaller scales and more flexibly, in which bacteria and archaea act to produce methane. These processes are being commercially developed, e.g. by Electrochaea. The efficiency of this route is around 82 %.

9.2. Application to grid scale storage

The production of hydrogen from low carbon electricity offers two main advantages. Firstly, hydrogen produced in this way can be directly used in other processes, offering a means of decarbonisation of other sectors. Secondly, large amounts of energy can be stored in relatively low volumes of hydrogen, when compared with other large scale energy storage media, such as CAES or PHS. Germany currently leads the way in terms of demonstrating the P2G concept, with 11 demonstration sites operating in 2013, ranging from 100 kW to 6 MW. The power of the system depends on the size of the electrolyser installed in terms of the charging phase, whereas the energy depends on the size of the hydrogen store. In the case of synthetic methane, this can be stored in existing natural gas pipelines and storage sites and hence is not treated separately here. In terms of electrical power on discharge (if this is the chosen option), this depends on how the hydrogen or synthetic natural gas is utilised. This could range from conversion in fuel cells at the kW to MW scale, to combustion in multi MW gas engines / turbines.

> Large amounts of energy can be stored in relatively low volumes of hydrogen, when compared with other large scale energy storage media, such as compressed air or pumped hydro.

9.2.1. Capacity of Hydrogen stores

Over 400 billion m^3 of natural gas are currently stored underground worldwide [62].

Hydrogen is already stored in salt caverns in the UK and USA. Hydrogen has over 200 times the volumetric energy storage density of PHS and 50 times that of compressed air, for example. Taking into account the fact that a typical large salt cavern field has a volume of 8×10^6 m^3, this would provide a hydrogen energy storage capacity of 1.3 TWh per field [63]. In summary, the use of salt cavern stores for hydrogen is considered essentially mature, with hydrogen stored at pressures up to 120 bar. Other potential hydrogen stores, such as depleted gas fields, rock caverns, aquifers and abandoned mine sites, require development to demonstrate that these could also be safely used.

9.2.2. Alkaline water electrolysers

Alkaline water electrolysers offer technology maturity and are commercially available. The cathode and anode materials in these systems are typically made of steel and nickel-plated steel, respectively. The liquid electrolyte is based on highly alkaline KOH. The energy conversion efficiency of electricity to hydrogen for current units is around 62-82 %. The main challenge in applying this technology to P2G applications is that current technology is not designed to provide the level of flexible response that this application requires and that power density is low, meaning that the system size is relatively large. Nor can high pressure hydrogen be delivered, which may be an issue depending on what the hydrogen is to be used for. That said, developers (such as Hydrogenics) are seeking to adapt the technology to deliver flexible operation, while maintaining lifetime.

Alkaline water electrolysers are a mature and commercially available technology, but challenges exist in matching their required level of flexible response and in improving their power density.

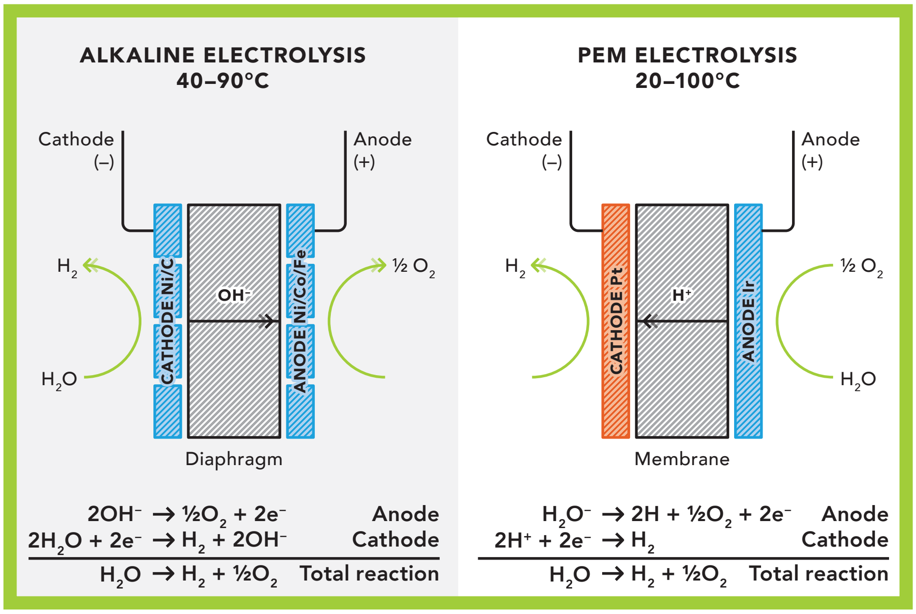


FIGURE 9.2
Schematic illustration of alkaline and Polymer electrolyte membrane (PEM) electrolysis cells [64].

9.2.3. Polymer electrolyte membrane (PEM) electrolysers

PEM electrolysers are emerging as a promising alternative to alkaline electrolysers. A leading developer of this technology is the UK company, ITM Power, who are developing this to the MW scale. This technology is commonly based around a polymer membrane and carbon electrodes catalysed with platinum group metal catalysts. As such, the technology is very similar to polymer fuel cell technology. A schematic illustration of both alkaline and polymer electrolysis is illustrated in Figure 9.2. The energy conversion efficiency of electricity to hydrogen is around 67-82 %. A key attraction of this approach is that pressurised hydrogen (to 80 bar) can be produced at a range of power levels from 10's kWe to MWe's and that the unit can respond flexibly within 1 second, making it a good fit to P2G applications. Furthermore, it is capable of high power densities which, coupled with the ability to operate at pressure, means that the system size is reduced compared with alkaline technology.

> PEM electrolysers offer high power densities, can produce pressurised hydrogen and respond flexibly within 1 second.

9.2.4. Solid oxide electrolysers

Solid oxide electrolysers are currently in the development stage. These build on solid oxide fuel cell technology, but take in electricity to split steam into hydrogen and oxygen. Their high temperature of operation offers much lower energy requirements for water splitting than the lower temperature alternatives and waste heat can also be recuperated to drive the endothermic steam electrolysis reaction, or the unit can be operated in thermo-neutral mode, where the heat requirement is balanced by internal heating within the electrolyser. A conversion efficiency of electricity to hydrogen of 100 % (or more) can be achieved, through heat recuperation. This electrolyser needs to be maintained at its operating temperature of 700-900 °C. When hot, fast response should be possible, but if allowed to cool, then start up times can be several hours, depending on the design and scale. The temperature of operation of solid oxide electrolysers means that co-electrolysis of steam and carbon dioxide to syngas is also possible, or the electrolysis of carbon dioxide to carbon monoxide and this could be attractive for the production of synthetic natural gas, or other fuels such as methanol.

> The high operating temperature of solid oxide electrolysers offers lower energy requirements for water splitting, co-electrolysis of steam and carbon dioxide to syngas and opportunities for recuperating waste heat.

9.2.5. Synthetic methane

Synthetic methane can be produced by combining hydrogen with captured carbon dioxide. This process requires a source of captured carbon dioxide, but has the advantage that it provides a potential closed cycle for carbon based fuels and that the synthetic methane produced can be readily used within the existing natural gas infrastructure. The main disadvantage is that additional costs and inefficiencies are introduced in the conversion steps. The most mature route is the Sabatier process. The process takes place at two temperature ranges: low temperature methanation in the range of 200–550 °C and high temperature methanation, operating between 550 and 750 °C. This is a large scale process, commercially available at the scale of 100's MW. The main challenge in terms of its application to grid scale storage is that it is not flexible, hence an additional buffer of hydrogen storage would be needed between the electrolyser and the plant. Biological processes are emerging which offer more flexible operation and operation over a greater range of power levels, offering an alternative route. Given an efficiency of around 70-85 % for these methanation processes, when coupled with the around 70 % efficiency of electrolysis, the overall conversion efficiency of electricity to synthetic methane is estimated at around 50-60 %. Overall round trip efficiency back to electricity depends on the conversion process used, but is likely to be around 30-35 % overall. Clearly, this is a relatively low round trip efficiency, but the main advantages here are the excellent fit of the approach to current infrastructure, the essentially unlimited storage capacity offered by the natural gas infrastructure, certainly in the UK, and the potential it offers for CO_2 utilisation, rather than CO_2 storage.

P2G offers potential for CO_2 utilisation, rather than CO_2 storage, closing the cycle for carbon based fuels.

9.3. Research needs for grid scale storage

In order to make P2G attractive for grid storage applications, key challenges in three main areas of research should be addressed: continued cost reduction of the electrolyser systems, extension of electrolyser lifetime and the development of more efficient and flexible electrolysers. In addition, attention needs to be paid to the demonstration of hydrogen storage in salt caverns and in the integration of electrolysis with CO_2 to produce synthetic methane, but these largely sit in the domain of engineering integration and technology demonstration, as much of the technology is commercially available, or approaching that point. As such, the research needs of electrolysis will be the focus here, with a particular focus on the emerging PEM and solid oxide electrolysers, as these appear to be most attractive for P2G applications.

Key research challenges include further cost reduction of electrolyser systems, lifetime extension, and the development of more efficient and flexible electrolysers.

9.3.1. Alkaline electrolysers

The main challenge here is developing a more flexible system, in which case attention needs to be paid to the development of more stable electrodes and membranes that prevent product gas cross over, limit operation at low loads for safety reasons and limit operation at elevated pressures.

9.3.2. PEM electrolysers

The key research challenges relate to understanding the fundamental processes driving performance and lifetime, as well as developing better materials and components offering lower cost and/or improved performance. In particular, it is important to reduce losses within the electrolyser to maximise its efficiency.

9.3.3. Electrocatalysts

To lower cost, there is benefit in continuing to reduce the loading of platinum group metal electro-catalysts by enhancing catalyst utilisation and/or to find alternate electro-catalysts that deliver equivalent performance and lifetime, but at lower cost.

9.3.4. Current collectors

To lower cost and/or increase lifetime, there is a need to develop more corrosion resistant current collectors and separator plates and/or to consider alternative designs in which both electrodes and current collectors are more closely integrated.

9.3.5. Membranes

Continued focus on developing longer life and lower cost membranes is necessary, for example, the hydrocarbon membranes being pioneered by UK company, ITM Power.

9.3.6. Stack design

Novel stack designs offering lower cost and greater scalability would benefit the technology by either lowering cost and/or allowing larger scale electrolysers to be constructed.

9.3.7. System Control

Validated models of operation, coupled with real time state of health monitoring, will support the development of appropriate control strategies for flexible electrolyser integration into energy systems.

9.3.8. Tools and diagnostics

Improved tools and diagnostic techniques to understanding the root causes of performance and lifetime loss are essential if we are to support the development of an electrolyser industry. These need to be used to inform the selection of materials, the design of components and the development of operating strategies.

9.3.9. Solid Oxide Electrolysers

The key research challenges here relate to improving the lifetime of materials used for construction and, in the longer term, developing stack and system concepts allowing operation at large scale. This work needs to be supported by improved understanding of the fundamental processes that determine performance and lifetime, through the development of new modelling tools and diagnostic techniques and, in particular, techniques allowing materials to be studied under realistic operating conditions: a challenge, given the temperature of operation. In particular, electrodes need to be developed for both anode and cathode that allow long term operation without degradation due to, for example, sintering, material loss, or chemical reaction with other components, such as the interconnects and electrolyte. Ideally, these electrodes would allow reversible operation, so that the same piece of equipment can be used in both electrolyser and fuel cell mode, offering a cost saving in some applications, though this is not needed for all concepts.

Suitable electrolytes exist to deliver the performance required, but improved understanding of their long term behaviour in electrolysis mode is needed and further optimisation of their mechanical properties would enable large cells to be produced. Improved interconnects need to be developed that are stable in the high humidity environment of the steam electrode and in the high oxygen environment of the air electrode. Better methods to monitor the state of health would support optimum operation and control of the technology. Finally, attention must be paid to developing better balance of plant components, in particular those related to thermal management such as heat exchangers and blowers.

10. Control and integration of grid scale storage

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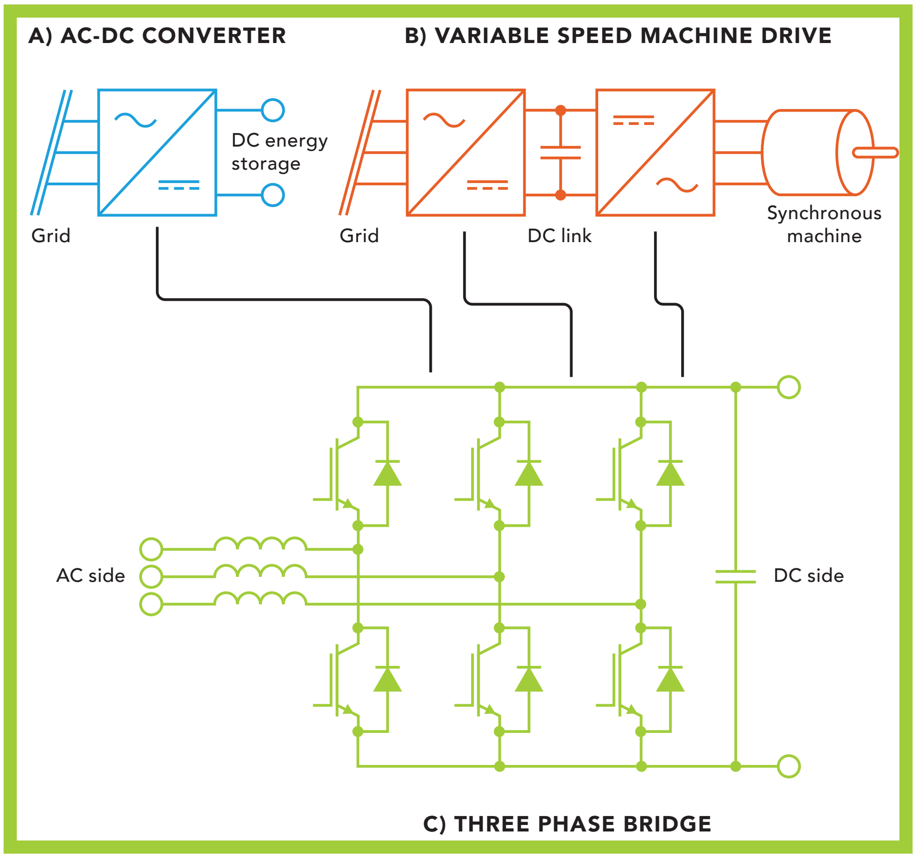
An energy storage system requires a grid interface coupled to a high-level decision-making controller to control power exchange with the grid, manage state-of-charge and monitor system health. In many cases, a power electronic circuit will form the grid interface, affecting overall system efficiency and reliability, as well as contributing to the capital cost of the system. The controller must operate the energy storage asset subject to system and grid constraints, in order to maximise return on investment. Developments in power electronic and control algorithm design promise to increase the effectiveness of a broad range of existing and emerging energy storage technologies.

FIGURE 10.1
Typical power electronic grid interfaces for energy storage systems.



10.1. Introduction to the technology

A large proportion of energy storage technologies available today have electrical outputs that cannot be directly connected to the AC grid, for example the DC outputs of batteries. These systems require a DC-AC power converter to interface with the grid, as shown in Figure 10.1a. Some energy storage systems have an inherently mechanical output (such as flywheels, compressed air and most types of thermal systems) and employ an electrical machine to convert stored energy to electrical energy and vice-versa. These systems often include a power converter acting as a machine interface, as shown in Figure 10.1b, because the mechanical output speed naturally varies over a charge / discharge cycle (e.g. flywheels). In other systems, it is often the case that allowing a variation in operating speed can increase the efficiency of the mechanical system, or reduce costs by allowing more compact machine design, e.g. high speed compressors for compressed air energy storage (CAES). This may give the impression that 'all storage systems need a power converter', but this is not always the case. Some energy storage systems connect to the grid using fixed-speed synchronous or induction machines, for example pumped hydro and some larger CAES systems [65]. In these cases, the power take-off shaft is constrained to rotate at a fixed multiple of the grid frequency that depends on the pole count of the electrical machine. Note that, although most individual energy storage technologies require (or greatly benefit from) the inclusion of a power conversion stage, systems without a conversion stage form the vast majority of currently installed energy storage capacity throughout the world, in the form of pumped hydro (20 GW in 2010 [66]).

10.2. Application to grid scale storage

10.2.1. Grid interfaces

In modern power systems, DC-AC and variable frequency AC conversion is invariably carried out by power electronic circuits, using solid-state semiconductor devices. The basic building block of low to medium power (10 kW - 1 MW) systems is the three phase bridge, shown in Figure 10.1c. This circuit is an AC-DC converter that uses six semiconductor devices, usually Insulated Gate Bipolar Transistors (IGBTs) to interface a three-phase AC source (left) to a DC source (right). These devices are operated in the switched-mode in order to minimise power losses. To connect two AC sources of differing magnitude, phase and frequency (e.g. a variable speed machine to the grid), two of these blocks can be connected back-to-back at the DC terminals, so that they present a three-phase connection on both sides. Through appropriate control of the IGBTs, arbitrary input and output voltages can be constructed using this circuit with few limitations, enabling very powerful and flexible control over the power exchanged between the left and right sides. Particularly, by constructing an AC voltage with the required phase and magnitude at the grid side of the converter, complete bi-directional control over the active and reactive power flowing into the grid can be obtained. At higher power (>1 MW), more complex circuits are used. These circuits typically contain a greater number of individually controllable semiconductor devices connected in series, allowing them to operate at the higher voltages associated with larger power converters.

> The three phase bridge uses Insulated Gate Bipolar Transistors, enabling very powerful and flexible control over the power exchanged between electronic circuits.

Energy storage systems using directly connected synchronous machines control power exchange with the grid using a governor and automatic voltage regulator, in the same manner as that for conventional power generation. Real power exchange is controlled by varying the mechanical torque applied to the machine shaft, while reactive power is controlled by varying machine excitation. Such systems have the distinction of contributing to the overall inertia of the grid, traditionally seen as an advantage because it tends to increase grid robustness during abnormal grid operating conditions (faults). Power electronic interfaces are capable of mimicking synchronous machine response to some degree, by the implementation of appropriate low-level controllers (a service often termed synthetic or emulated inertia [67, 68]), but are typically much more limited in the level of fault current they can provide. Power electronics-interfaced energy storage systems will therefore tend to be less capable of providing support during periods of extreme grid stress than their synchronous, machine-interfaced cousins.

> Energy storage systems using power electronics will tend to be less able to support grids during abnormal operating conditions.

10.2.2. Control of energy storage systems

Fundamentally, the grid interface of an energy storage system provides the ability to manage active and reactive power exchanged between the system and the grid. The grid interface obeys a power order made by the next level of an overall control hierarchy, as shown in Figure 10.2. A high-level controller will integrate a wide range of input information and seek to fulfil particular power system services. For example, on a distribution network, the high-level controller may primarily be performing night-day energy arbitrage, but may also provide peak shaving services to alleviate stress on an overloaded network transformer, while also contributing to local voltage control to smooth out voltage fluctuations caused by intermittent load and generation (EV charging, photovoltaics, wind, etc.).

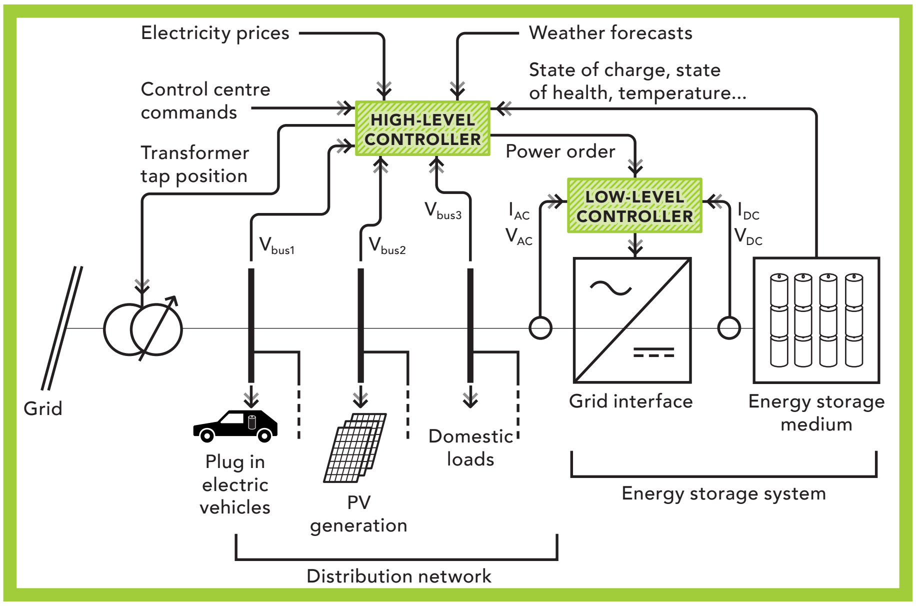


FIGURE 10.2
An energy storage system operating on a distribution network. A range of information must be integrated by the high-level controller, in order to effectively operate the energy storage resource. The energy storage system may also operate in conjunction with other equipment on the network, in this case an on-load tap changing transformer.

The controller may also be sensitive to wider grid-level conditions, for example it may be required to respond to grid frequency deviations in order to provide power balance during times of load / generation mismatch (reserve services). Fundamentally, all these services are provided by varying the real and reactive power orders made to the low-level control system on a moment-to-moment basis. However, choosing power orders over long periods of time to maximise some measure of utility (earnings) is a complex problem: future demand is uncertain, but decisions made now will affect the energy stored and therefore the ability to act at a later date [69, 70].

> Future demand is uncertain, but decisions made now will affect the energy stored and therefore the ability to act at a later date.

10.3. Research needs for grid scale storage

10.3.1. Power converter cost, power rating and efficiency

The power electronic grid interface contributes a relatively large fraction of a complete energy storage system's cost. The contribution of the power converter to system capital cost varies considerably depending on scale, ranging from 13 to 33 % for a 10 MW and 25 kW Li-ion system, respectively [71]. There is a significant economy of scale attached to power converter equipment costs, as indicated by Figure 10.3. The contribution of the power converter to energy losses, and therefore operating costs, can also be significant. Depending on power rating, peak one-way power converter efficiencies of 97 % are common, but this headline figure tends to underestimate converter contribution to losses when often-poor capacity factors are taken into account. A property of power electronic systems is that their rating and size depends almost completely on the peak power they must process, not the average power. This means that for power-rich but relatively energy-poor storage technologies, such as supercapacitors, the grid interface may become a very significant fraction of overall system cost. Conversely, for energy-rich, power-poor base-load type applications, such as flow cells, the power electronic grid interface may be expected to be only a small part of total system cost. While some of these challenges are faced by other grid power electronic systems (notably wind turbine converters and photovoltaic inverters), the particularly 'peaky' nature of typical energy storage applications makes techniques for flattening the efficiency-power curve and designing for the anticipated load cycles important. Advances in semiconductor and passive component technologies, particularly the transition to wide band gap semiconductor devices, will tend to increase efficiency, while also allowing equipment footprint to be reduced [72].

> The rating and size of power electronic systems depends on the peak power they must process, not average power. For energy-rich, power-poor storage technologies, the power electronic grid interface forms only a small part of total system cost.

10.3.2. Scaling to larger system sizes

The largest monolithic converters on the market today are found in the latest generation of wind turbines (up to 8 MW in the Vestas V164). However, there are opportunities to connect energy storage systems to the upper-distribution and transmission networks. This may mean that larger power electronic systems are desirable. This may be achieved in two ways: (i) an increase in unit size, necessitating advances in circuit design and component technology, or (ii) by the paralleling of many smaller units, requiring research into interconnection options and control systems. For very large systems, techniques used in gigawatt-scale high voltage direct current (HVDC) converters may be usefully transferred into the energy storage arena.

FIGURE 10.3

Scaling of power converter equipment costs, based on data from [71]. Equipment costs do not include power converter installation cost or costs associated with the physical connection to the grid (these costs can be significant, but depend strongly on the specific project).

10.3.3. Specialised power electronics for cell-based storage

Batteries and supercapacitors provide energy storage in discrete units of a fixed size. These units are typically very small compared to the rating of typical grid applications, for example even the largest single Li-ion cells available today store less than 1 kWh each and ratings of nearer 100 Wh are more common. Typically cells are connected in series strings (called packs) to increase their output voltage and provide larger storage units for interfacing to the grid. However, a weak cell in the pack can reduce the overall capacity and power delivery capability of the pack, while a failure of one cell can effectively remove the entire pack from the energy storage system. For this reason, cell manufacturers have very high quality control standards and extensive testing procedures in place to reduce the probability of individual cell failure, but with a penalty in terms of manufacturing yield and costs. Modular Multi-Level (MML) power electronic circuits provide an alternative way to integrate a large number of cells in a circuit by effectively interfacing each cell to the wider system using a small dedicated power electronic circuit that also performs the DC-AC conversion process. The participation of each cell in the overall energy storage system can then be controlled in a very fine-grained manner, allowing the maximum storage potential of each cell to be extracted. Weaker cells can be used more lightly and failed cells can be bypassed, removed and then replaced without interrupting normal operation. This provides two main benefits. Firstly, scaling to larger systems and the subsequent requirement to deal with frequent cell failure becomes conceptually much simpler. Secondly, because the system is inherently capable of dealing with cell-to-cell variation, cell manufacturing tolerance can be relaxed, potentially leading to reductions in cell cost. The application of MML circuits to energy storage systems is currently an active area of research [73, 74].

> Modular Multi-Level power electronics enable integration of a large number of cells in a circuit, enabling fine-grained control of each cell's participation in the overall energy storage system.

10.3.4. Control systems for grid support

Low-level control of power electronic grid interface converters and synchronous machines is well understood. However, as the grid penetration of energy storage systems increases, it becomes critical to ensure that their behaviour is well defined and modelled under abnormal conditions, such as voltage depressions, frequency deviations, etc. in order to ensure continued grid stability and security. Such behaviour is often referred to as fault ride through capability, especially when applied to power electronic converters. In addition, energy storage systems offer the opportunity to support islanded operation of parts of the grid for short periods of time, which although technically challenging to manage, could offer significant security and resiliency benefits under some conditions. Particularly, all types of energy storage system are naturally suited to providing black-start facilities.

> Energy storage systems offer the opportunity to support islanded operation of parts of the grid for short periods of time, offering significant security and resiliency benefits, for example black-start capability.

10.3.5. High-level control of energy storage

Effective high-level control of an energy storage system is a challenging task. The problem is non-linear and time-varying, with large, built-in uncertainty. The fundamental constraints are system energy and power capacity. However, many second-order system properties must be taken into account, including round-trip efficiency, energy leakage rates (e.g. imperfect insulation in thermal storage systems) and degradation of the storage medium (e.g. capacity fade of batteries), all of which can depend on state-of-charge, instantaneous power demand, cycle number, operating history and environmental conditions [75, 76]. Balancing each aspect of system behaviour to extract maximum value requires a thorough understanding of the dominant physical mechanisms contributing to each effect and a theoretical and computational framework for delivering a solution. The most appropriate control strategies will vary depending on the particular strengths and weaknesses of the technology they are applied to and the position of the system on the grid. Continuing research applied to the control and management of new energy storage systems is essential in order to deliver the expected benefits of energy storage technology.

> Balancing each aspect of system behaviour to extract maximum value requires a thorough understanding of the dominant physical mechanisms.

10.3.6. Aggregation of small energy storage systems on the distribution network

A particular control challenge arises on the distribution network where very large numbers of small-scale energy storage systems may be installed. It has been suggested that, per unit energy stored, energy storage located on the distribution network delivers the highest utility, mostly because it can reduce the requirement for distribution network reinforcement. Aggregation of many small systems, such that they behave in a way to benefit both the grid and their owners while limiting the control overhead placed on the grid operator, is an active area of smartgrid research [77]. This work has many synergies with demand side response and vehicle-to-grid (V2G) research areas.

11. Conclusions

It is evident that the UK, as an island nation with ambitious carbon reduction targets, will place increasing value on the flexibility offered by energy storage to manage its transition to a low carbon energy system. It is also clear that no single energy storage technology will meet the needs of the future energy system, with a range of services requiring a range of storage characteristics, from the rapid delivery of power in a matter of seconds, through to longer term energy storage over hours, days or weeks. It is also clear that the UK has significant research strengths across a number of the potentially critical energy storage technologies and their integration, along with innovative companies seeking to develop, demonstrate and commercialise energy storage solutions.

The report sets out the views of the authors on the critical research needs facing this sector, if we are to deliver cost effective storage solutions in an appropriate timescale. The report does not seek to set out the market or regulatory barriers that face the sector today, though these are clearly also important barriers to success. What is clear is that we need to learn by doing today, to scale up and re-risk promising technologies, as well as develop our strategies to interface and control storage technologies. In addition, we need to support the underpinning research that will continue to drive down cost and increase lifetime in the future, both by improving today's storage solutions and by developing new solutions based around alternate chemistries, materials and/or concepts.

In terms of the different storage technologies themselves that have been considered here, we can draw the following conclusions. For the past two decades, research has grown in the sector of Li-ion batteries and our knowledge of the battery chemistries has deepened. Although we have a better understanding of the interphase chemistry between the electrolyte and the electrode surface, research in those areas needs to be pursued due to the appearance of new battery chemistries in both lithium and sodium-ion batteries. The understanding of the mechanisms for the formation and the growth of the SEI, as well as the ion transport across it, is fundamental to the enhancement of the battery performance. Most anode materials are based on carbon exhibiting good cycling stability, however, they have a limited lifetime that may not be sufficient for the future generation of higher endurance batteries; thus, new anode materials of high specific capacity such as alloys or metal oxides have to be sought.

Regarding the cathodes, higher capacities of lithium and sodium-ion batteries can be achieved by developing new electrode chemistries and understanding the intercalation phenomenon. Intercalation electrode materials can undergo structural transformations during lithiation / delithiation or sodiation / desodiation; these structural changes need to be investigated and, once understood, will allow us to design strategies for improvement of the electrochemical performance. In some ways, Na-ion batteries are facing identical scientific challenges to Li-ion batteries, as both operate with a similar chemistry. Since the sector of Li-ion batteries has observed considerable developments in anodes, cathodes and electrolytes, it can serve as a springboard to rapid progress in Na-ion batteries. It is the role of researchers to find an adequate balance between electrode performance, cost and safety.

Aqueous based batteries already have a significant share of the battery market, in particular lead acid, offering a number of potential advantages for grid scale storage, such as low cost and safety. The challenge here is to translate this chemistry into battery forms suited to grid scale storage applications, with its requirements for long life and multiple cycles. Of the various cell forms under development, nickel-iron cells are probably the most promising of all Ni-based technologies, for large scale energy storage. Other promising aqueous based batteries are copper-zinc, zinc-air and aqueous lithium ion "rocking-chair" batteries. All these offer the potential for large scale and low cost batteries, but all require further development to realise this potential.

The grid scale applications of supercapacitors requires primarily a reduction in cost, as well as an improvement in energy density, without compromising power density, high frequency response or high cycle life. Because grid storage installations are static, previously uncompetitive materials in terms of their per unit weight performance, including aqueous based systems, become feasible if they can offer valued, new combinations of power, energy, cost, lifetime, safety and environmental compatibility. A systems design approach is needed, where electrode combinations based on low cost materials are matched carefully with electrolytes, while new fabrication technologies should be developed, allowing full and effective exploitation of these electrochemical systems, at a scale relevant to grid storage demands.

Redox flow batteries offer an attractive storage option when several hours of energy storage are required. The key challenges today relate to cost reduction, reflecting the cost of the most commonly used vanadium electrolyte, the power cell and the auxiliary plant. Another challenge is the relatively low power density achieved in the power stack, meaning that large amounts of high cost ion exchange membranes are required, as well as other cell materials. The third key challenge is the relatively low energy density of the electrolyte. As well as seeking to improve vanadium flow batteries, there has been a surge of interest in new flow battery chemistries in the past ten years, aimed at lowering cost and/or increasing energy density.

The successful deployment of compressed air energy storage requires cost reduction through improved means of preparing suitable salt caverns for air storage, innovation in turbo-machinery design and improved round trip efficiency through process integration and heat recovery. The latter point is coupled with advances in thermal storage materials and technologies.

A number of exciting energy storage concepts are based around the storage of heat and/or cold. For all these technologies, there is a need to understand the relationships between properties and behaviour of thermal energy storage materials, components, devices and systems, as well as how the manufacture processes of the materials, components and devices affect these relationships. There is also a need to develop lower cost balance of plant for these systems, such as heat exchangers, which are critical to their performance.

In order to make P2G attractive for grid storage applications, key challenges in three main areas of research should be addressed: continued cost reduction of the electrolyser systems, extension of electrolyser lifetime and the development of more efficient and flexible electrolysers. In addition, attention needs to be paid to the demonstration of hydrogen storage in salt caverns, as well as the integration of electrolysis with CO_2 to produce synthetic methane. Research challenges depend on the electrolyser technology and its technical maturity, but continued lifetime extension and cost reduction remain priority areas for all electrolyser types.

Finally, it is important that attention is paid not only to the storage technologies themselves, but also to their integration and control in the energy system. An energy storage system requires a grid interface coupled to a high-level decision-making controller to control power exchange with the grid, manage state-of-charge and monitor system health. In many cases, a power electronic circuit will form the grid interface, affecting overall system efficiency and reliability, as well as contributing to the capital cost of the system. A property of power electronic systems is that their rating and size depends almost completely on the peak power they must process, hence for power-rich but relatively energy-poor storage technologies (e.g. supercapacitors), the grid interface may become a very significant fraction of overall system cost. The most appropriate storage control strategies will vary, depending on the technology they are applied to and the position of the system on the grid. Continuing research applied to the control and management of new energy storage systems is essential in order to deliver the expected benefits of energy storage technology.

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