Subsurface Flow Batteries: Concept, Benefits and Hurdles

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Abstract: We introduce a novel concept for storage of electrical energy in the subsurface—storage of flow-battery electrolytes in porous rock. Flow-batteries operate by electrochemical transformations of electrolytes, rather than of electrodes, and their energy capacity can therefore be increased indefinitely by using larger electrolyte tanks. Saline aquifers may be the cheapest way to provide large-scale storage for this purpose. Storage would be within high-porosity, high-permeability reservoirs sealed by impermeable layers but—in contrast to hydrocarbon, H_2 or CO_2 storage—electrolytes would be trapped at the base of such formations as a consequence of their high density compared to natural brines.

Calculations show that the resulting devices may be able to charge/discharge safely, cheaply, efficiently and continuously for weeks at 100's of MW. Hence they are a possible solution to the problem of long-term renewable energy intermittency. We discuss a range of electrochemical, geochemical, microbiological and engineering hurdles which must be overcome if subsurface flow-batteries are to become a practical technology. No insurmountable problems were found in our preliminary assessment but further laboratory studies are needed.

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Renewable energy is now cheaper than fossil-fuels for electricity generation (IEA 2020) but it cannot yet be used for all society's generating needs because of intermittency. Existing electrical storage systems can manage short-term problems such as frequency-control and demand management on scales from seconds to hours (Renewable Energy Agency 2017) but there are also longer-term issues. For example, NW Europe occasionally experiences periods of several weeks with simultaneous low sunshine and low wind (Huneke *et al.* 2017). The obvious solution is a long-term electrical storage system. Unfortunately, existing technologies do not have the necessary combination of high efficiency, high capacity, long-term storage and low-cost needed to allow economically viable storage over weeks to months (IRENA, 2017).

Subsurface H_2 storage and/or compressed-air energy storage (CAES) may be solutions to these problems but this paper looks, for the first time, at whether subsurface flow batteries (SFBs) could also be a way forward.

Flow batteries differ from traditional batteries by using electrochemical transformations of electrolytes rather than of electrodes (Park *et al.* 2016). As a consequence, they can provide high energy-capacity at low cost if large, cheap electrolyte tanks are available. This paper considers whether porous-rock reservoirs are suitable storage locations (see Fig. 1). Electrolyte storage in porous reservoirs is a novel concept although several energy companies are considering storage of electrolytes in salt caverns (EWE, 2017; RWE, 2020).

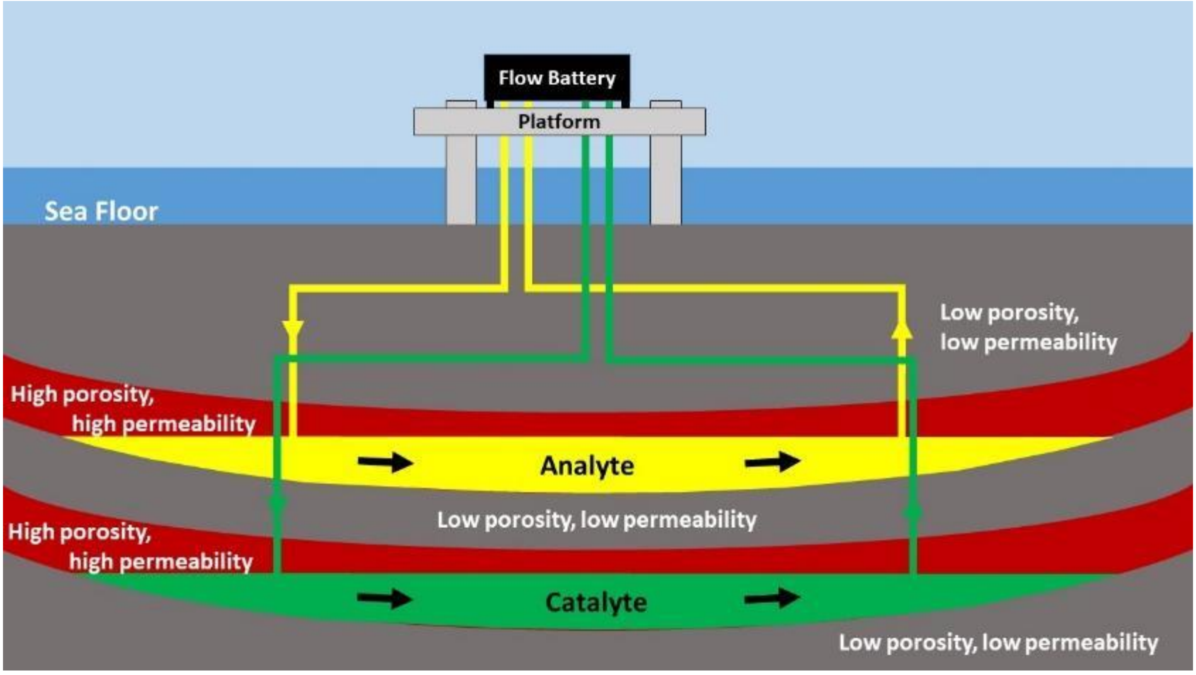

Figure 1. The subsurface flow-battery concept. Low-cost, high-capacity electrolyte storage (for a flow battery) is provided by porous reservoirs. Electrolyte density will be higher than that of natural brines and, hence, storage will be at the base of the reservoirs with an underlying "cap" rock.

The next section looks at the theoretical energy efficiency, storage capacity and charge/discharge power of SFBs. This highlights their potential advantages but we then discuss a range of electrochemical, geochemical, microbiological and engineering hurdles that must be overcome if SFBs are to become a practical technology. We finish the paper with a brief look at costs compared to existing electrical storage technologies. Hence, this paper gives an initial assessment of whether SFBs could be technically, environmentally and economically viable as a solution to renewable energy intermittency.

Theoretical Performance

As shown in Fig. 1, two electrolytes (analyte for the anode and catalyte for the cathode) are stored in two separate subsurface regions. For illustrative convenience they are shown, in Fig. 1, as separated vertically but horizontal separation within multiple synclines of the same formation is also possible.

For the flow-battery itself, there are many different designs utilising many different electrode and electrolyte chemistries. This paper concentrates on the specific case of the all-iron flow battery (Hruska and Savinell 1981). The chemical reactions in the two halves of a discharging all-iron cell are

$$2FeCl_3 + 2e^- \rightarrow 2FeCl_2 + 2Cl^- \quad (1)$$

$$Fe + 2Cl^- \rightarrow FeCl_2 + 2e^- \quad (2)$$

The first reaction occurs within a mixed $FeCl_3/FeCl_2$ electrolyte whilst the second reaction involves dissolution of an iron-electrode into an $FeCl_2$ electrolyte. The chloride ions generated in reaction (1) diffuse across a membrane separating the two half-cells to provide the chloride ions consumed in reaction (2). Overall electrical balance is achieved by flow of electrons from reaction (2) to reaction (1), i.e. the generated electric current. Reactions (1) and (2) are reversed if the battery is charged rather than discharged.

Note that, since this design involves dissolution and re-plating of an iron-electrode, this is a hybrid battery rather than a pure flow-battery. However, there are good reasons for this choice. Ferrous ions and chloride ions are common constituents of subsurface brines (e.g. see Munz et al., 2010) and, hence, this particular flow-battery chemistry is environmentally benign. Iron chlorides are also low cost and widely available at industrial volumes since they are used for sewage treatment. Low cost and low environmental impact are our reason for choosing the all-iron flow-battery in this preliminary assessment of SFBs although most of our conclusions apply, or can be extended, to other flow battery designs.

Electrolytes will need to have high ion concentrations (compared to natural brines) in order to store significant energy and, hence, they will be relatively dense and sink to the base of the reservoir formation (as shown in Fig. 1). This leads to the first advantage of SFBs; electrolyte storage will be in synclinal structures sealed by underlying low-permeability formations. In contrast, CO_2 and H_2 subsurface storage are in anticlinal structures and so SFBs will not compete for the same storage locations. Furthermore, accidental leakage can be contained simply by shutting the pumping system down allowing dispersion of the harmless iron and chlorine into the deeper subsurface.

However, SFBs are only useful if they can store/discharge electricity at high enough power. Furthermore, if they are to be used for longer-term storage, they must have a large energy-storage capacity. A combination of potential-flow theory and Darcy's law allows a first pass estimate of these quantities. This approach has been widely used to model subsurface flows for many decades (e.g. see King Hubbert, 1957).

Potential-flow theory assumes that slow, steady flows are irrotational and, hence, that velocity can be represented as the gradient of a potential field, i.e.

$$\mathbf{u} = \nabla \Phi \quad (3)$$

where **u** is the flow velocity and Φ is potential. The simplified case of simultaneous injection and extraction of electrolyte using two perforated, vertical wells in a horizontal layer—of constant thickness, porosity and permeability—can then be modelled as a 2-dimensional potential flow, from a point source into a point sink, with a potential of

$$\Phi = (Q/4\pi) \ln[((x+a)^2 + y^2) / ((x-a)^2 + y^2)] \quad (4)$$

for a source at location $x=-a$, $y=0$ and a sink at location $x=+a$, $y=0$. Here, Q is the sink and source strength given by

$$Q = F/\varphi h \quad (5)$$

where F is the volume flux (m^3/s), φ is porosity and h is layer thickness. An alternate formulation (Darcy-flow of a viscous fluid through a porous medium) gives a flow velocity of

$$\mathbf{u} = (-k/\mu\varphi)\nabla P. \quad (6)$$

Here, k is permeability, μ is viscosity and P is pressure. Comparison of eqns (3) and (6) then implies

$$P = (-\mu\varphi/k)\Phi + P_b \quad (7)$$

where P_b is a background pressure. Combining eqns (4), (5) and (7) gives the excess pressure field as

$$\Delta P = P - P_b = -(\mu F/4\pi kh) \ \ln[((x+a)^2 + y^2) / ((x-a)^2 + y^2)]. \quad (8)$$

The injection pressure is the excess pressure at the injection well radius, i.e. at

$$(x+a)^2 + y^2 = r_w^2. \quad (9)$$

Hence, the excess pressure around the injection well is

$$\Delta P = -(\mu F/4\pi kh) \ \ln[r_w^2/ (r_w^2 - 4ax)]. \quad (10)$$

But $r_w << a$ and $x \approx -a$. Hence,

$$\Delta P = (\mu F/4\pi kh) \ \ln[4a^2 / r_w^2]. \quad (11)$$

The key quantity in this expression is the volume-flux, F. This flux can be combined with the energy density, ρ_e, to give the device power. This energy density is defined, for electrochemical devices, as the maximum energy stored divided by the volume of the entire device which, for a flow-battery, is dominated by the combined volume of the two electrolytes. Hence, rearranging eqn (11) for volume-flux of both electrolytes combined (i.e. $2F$) and introducing the energy density of the electrolyte leads to

$$\text{Power} = 2F\rho_e = 8\pi\Delta Pkh\rho_e / \mu \ln[4a^2/r_w^2]. \quad (12)$$

Equation (12) is a key indicator of SFB performance. For example, a maximum safe excess pressure of 2 MPa, a permeability of 2D ($=1.97\times10^{-12}$ m^2), a reservoir thickness of 100m, an energy density of 475 MJ/m^3 (≡132 Wh L^{-1} (Hruska and Savinell 1981)) a viscosity of 4×10^{-4} Pas (appropriate for a water-based electrolyte at 2km depth, (Likhachev 2003)), a well separation of 300 m (i.e. a=150m, see later for justification) and a bore-radius of 0.1m gives a power of 736 MW.

This is encouraging. For comparison, the London Array (the world's largest offshore wind-farm when completed in 2013) has a capacity of 630 MW. The SFB installation described above would therefore be more than capable of providing back-up to a wind-farm of London Array size.

Power-levels therefore look useful but the facility should also store sufficient energy to provide backup over an extended period. This capacity will be controlled by the size of subsurface containment structure and that will be site-specific. However, an order of magnitude estimate can be obtained from the time taken for electrolyte to travel from the injection well to the extraction well. This can be thought of as the time to “fill” or “empty” the reservoir since, after that time, partially (or fully) charged/discharged electrolyte will start to appear at the “wrong” well. In practice, the charge/discharge can continue beyond this point with little loss of performance since electrolyte will also be travelling along less direct routes. Hence, the minimum travel time provides a lower-limit for the true charge/discharge time.

The minimum time is found by restricting interest to the direct line between the source and sink so that eqn. (4) simplifies to

$$\Phi(x) = (Q/4\pi)\ \ln[\,(x+a)^2 / (x-a)^2\,]. \tag{13}$$

The velocity along this line is

$$\begin{aligned} u(x) &= \partial\Phi / \partial x = Qa / \pi(a^2-x^2) \\ &= Fa / \pi\varphi h(a^2-x^2) \end{aligned} \tag{14}$$

giving a travel time from source to sink of

$$\begin{aligned} t &= \int_{-a}^{a} \frac{dx}{u} \\ &= 4\pi\varphi h a^2 / 3F. \end{aligned} \tag{15}$$

Substitution of F, using eqn (11), allows eqn. (15) to also be expressed as

$$t = (\varphi\mu a^2 / 3k\Delta P)\ \ln[\,4a^2/r_w^2\,]. \tag{16}$$

Equation (16) gives a charge/discharge time of 14 days for parameter-values as before and 10% porosity. This SFB configuration could therefore provide a few weeks’ backup during periods of simultaneously low sunshine and wind. Larger well separations increase this storage time rapidly. For example, a separation of 1 km (a=500m) would provide 180 days of storage, i.e. sufficient for seasonal balancing (e.g. storing excess solar energy in summer and discharging it in winter). However, for reasons we come to at the end of this paper, we will concentrate on the a=150 m system.

The volume capacity of the resulting system is obtained from a rearrangement of eqn. (15) to yield

$$Ft = 4\pi\varphi h a^2 / 3 \tag{17}$$

with a corresponding energy capacity of

$$2Ft\rho_e = 8\pi\varphi h a^2\rho_e / 3 \tag{18}$$

Where the factor of 2 is introduced, as before, because the system is simultaneously pumping two electrolytes and ρ_e is the power density for the combination. For the same parameter-values as before, this equates to 249 GWh. For comparison, the largest pumped hydro storage system, in the UK, is the Dinorwig Power Station in north Wales with an energy storage capacity of 9.1 GWh (Scottish Renewables 2016). This illustrates a key advantage of SFBs over the well-established technology of pumped-hydro—SFBs have much higher energy capacity and, hence, can provide electricity backup for much longer periods of time.

The implication of these preliminary results is that SFBs could provide electricity storage with sufficient charge/discharge power and sufficient energy-capacity to be useful. In addition, SFBs have a number of possible advantages over H_2 storage and CAES.

Firstly, the safety advantage already discussed (accidental leakage is environmentally benign) is enhanced by the near-constant storage-volume and temperature resulting from extracting charged/discharged electrolyte whilst simultaneously injecting discharged/charged electrolyte back into the same reservoir. This reduces the risk of containment failure since it avoids the thermo-mechanical stresses produced by the charge/discharge cycles of H_2 and CAES storage (e.g. see Böttcher et al., 2017 on H_2 storage in salt caverns). The negative relative pressure in the extraction half of the system also helps to maintain integrity.

Flow batteries also have round-trip energy efficiencies (i.e. output energy/input energy) in excess of 80% (Tang *et al.* 2013). This compares favourably with <40% for H_2 electricity storage (Pfeiffer and Bauer 2015) and ~50% for existing CAES systems (Jafarizadeh *et al.* 2020) although it should be mentioned that adiabatic CAES may allow this to increase to >60% (Hartmann *et al.* 2012).

However, this high efficiency would be undermined if SFBs consumed significant energy in pumping viscous electrolytes through the porous subsurface. Note that energy-loss has the same units as ρ_e (i.e. energy loss for each m^3 of electrolyte pumped) and should be significantly smaller than ρ_e as we do not want to consume a significant fraction of the energy stored. Note also that energy densities have units of pressure ($J/m^3 \equiv Pa$) and, in fact, the pumping-loss energy density is simply the pressure drop from injection to extraction well. For the parameters used above, this is 4 MPa ($\equiv$4 MJ/m^3, NB due to +2MPa at injection and -2MPa at extraction) compared with a storage energy density of 475 MJ/m^3. Hence, energy loss during pumping will only reduce the round-trip efficiency by about 2% (N.B. we are pumping two electrolytes and so total losses are 8 MJ/m^3).

A final theoretical advantage is the simplicity of SFBs. The same device is used for both charge and discharge and there are relatively few moving parts and no high-temperature components. Hence, SFBs are likely to be reliable and cheap to operate.

In summary, SFBs look promising from power, storage-time, safety, reliability and efficiency points of view. But these are theoretical expectations. In practice, there are significant hurdles to achieving this performance and we now turn to these.

A Preliminary Discussion of Possible Problems

This section takes a first look at issues that may make SFBs less effective than the foregoing analysis suggests or that may make SFBs too expensive to build. We start by estimating the size of flow-battery required to achieve the performance set out in section 2. Is it unrealistically large?

The size of any battery is controlled by the power collected/produced by each square metre of electrode during charging/discharging (the power density). Tucker et al (2015) give a value of 180 W/m^2 for their all-iron flow-battery. A practical device might therefore consist of banks of, say, 1kW cells each with an electrode area of ~5m^2. The thickness of each of these cells is hard to specify at present but is unlikely to differ greatly from ~0.1m to give each 1kW cell a volume of order 0.5m^3. Hence, the SFB described in section 2, with a power output of 736 MW, would consist of cells with a total volume of 368 000 m^3. This could be contained in a cube of side 72 m and is similar to the enclosed volume of the superstructure of a large offshore oil-rig, i.e. it's challenging but not impossible. Furthermore, electrodes can be constructed with high surface areas (e.g. hierarchically structured electrodes, (Gabardo *et al.* 2013)) and these may allow substantial reductions in cell volume.

Higher power densities may also be possible. Gong et al. (2016) report all-iron flow-battery power densities of up to 1.6 kW/m^2 when using triethanolamine and cyanide anions in place of Cl^-. Unfortunately, these alternate anions have significant cost and environmental disadvantages and this order-of-magnitude improvement in volume only reduces device linear dimensions by a factor of 2.

Another relevant factor is the possible need to cool the cells. This could require pumping of coolant with consequent increases in device volume and complexity. Fortunately, this does not appear to be an issue. If we assume 10% energy losses on charging and 10% energy losses during discharging (i.e. an 80% round-trip efficiency) and that the energy losses occur as low-grade heat which warms the electrolyte, then, from the definition of specific heat capacity, c, the expected warming, ΔT, is

$$\begin{aligned} \Delta T &= \Delta H / cM \\ &= 2\rho_e F\eta t / 2c\rho Ft \\ &= \rho_e\eta / c\rho \end{aligned} \tag{19}$$

where ΔH is heat input, M is mass, η is efficiency and t is time. Assuming ρ_e=475 MJ/m^3, η=0.1, c=4.2 kJ/K/kg and ρ=1000 kg/m^3 then gives ΔT=11K. This can easily be absorbed by the electrolytes; especially as they will have cooled from their subsurface values (~60 °C for a 2 km deep reservoir) as they were pumped up from depth and into the flow-cell.

The key development issues are therefore to minimize cell thickness and maximize power-density and electrode-area whilst retaining low-cost, environmentally-benign electrolytes. Building a prototype cell is the obvious first step.

The next problem we consider is that the maximum rate at which electrolyte can be pumped is constrained by the physics of porous reservoirs and so, to achieve high powers, the electrolyte must have high energy density. Unfortunately, achieved values are significantly lower than theoretical ones for the all-iron design. Tucker et al. (2015), for example, only achieved a density of 11.5 Wh/L (≡41.4 MJ/m^3)—an order of magnitude less than assumed in section 2. This brings the SFB estimated power down to 64 MW which may not be high enough to make such a system economic.

Yu et al. (2021) achieved a significantly better energy density of 32 Wh/L (≡115 MJ/m^3), using sulphate anions in place of chlorine, but this required addition of 1-ethyl-3-methylimidazolium chloride to enhance sulphate solubility. The cost and environmental implications of the Yu et al (2021) design therefore require further investigation although it is worth noting that sulphate ions are benign since they are naturally present in subsurface brines.

Other ways forward, if energy densities are unavoidably low, is to increase the driving pressure and/or the reservoir permeability. There is some scope to increase pressure (e.g. by using deeper reservoirs) but this is ultimately limited by the efficiency issues discussed earlier; a 4 MPa pressure drop implies almost 20% energy losses due to pumping (if the energy density is only 41.4 MJ/m^3) and this deteriorates further as pressure is increased. An alternative approach is to increase permeability using hydraulic fracturing (Valkó 2014).

Another way to tackle issues of low power density is simply to sink more wells, either into the same reservoir zone or, possibly, into a number of separate electrolyte ponds. This obviously increases costs. Horizontal drilling would also increase flow rates significantly (e.g. it has been used to obtain high rates of CO_2 injection at Sleipner (Kongsjorden *et al.* 1998)).

Hence, low-energy density is unlikely to be an insuperable barrier to SFB deployment. Further research should bring energy densities up (current values are far below the theoretical maximum) and use of multiple wells, horizontal drilling and hydraulic fracturing should enable significant enhancements to the pumping rates given by the simplistic, single-source, single-sink, 2D modelling of section 2.

All the power and energy density issues, discussed to this point, will be important regardless of the flow-battery chemistry adopted. However, the all-iron configuration suffers from an additional, specific problem—"parasitic" hydrogen generation, i.e. generation of some hydrogen gas, instead of metallic iron, when reaction (2) is reversed. This reduces the round-trip efficiency of the cell but it will be supressed by the moderately high temperature of sub-surface stored electrolyte and can be supressed further by additives (Jayathilake *et al.* 2018). A more radical solution is to regard hydrogen generation as an opportunity rather than a problem! The SFB could be operated as a hybrid electrical-storage and H_2 generation device and, if a hydrogen-economy develops over the coming decades, selling parasitic hydrogen may be more cost-effective than preventing its generation.

The problems discussed so far are relevant to all-iron flow-batteries even if artificial, surface storage tanks are used but the subsurface nature of our proposed SFBs introduces a number of unique problems. The first of these is that electrolytes will inevitably be contaminated by contact with mineral surfaces, diluted by pore-fluids and metabolised by microbes in the subsurface. We need to determine whether these interactions will significantly reduce flow-battery performance.

Some chemicals present may actually help (for example, NaCl is frequently used as a supporting electrolyte in flow batteries (e.g. Mundaray et al. (2021)) but other contaminants could result in unwanted side-reactions that consume reactants needed for reactions (1) and (2) or that lead to Fe loss and precipitates (e.g. iron oxides, hydroxide, and FeOOH) blocking pore-spaces and preventing electrolyte flow. However, some precipitates such as calcite or quartz may also be useful as they will predominantly form at the brine/electrolyte interface and, hence, help seal off the electrolyte from the brine. Detailed experimental investigations and geochemical modelling bringing electrolytes into contact with realistic brine chemistries and mineral surfaces will allow progress on understanding these issues.

Another major concern is electrolyte loss that depends on thermodynamic stability of injected $FeCl_3$ in brine. Aqueous $FeCl_3$ solution is stable at a very low pH but the speciation of aqueous Fe^{3+} changes after mixing with a slightly alkaline brine solution in the subsurface. For example, a complete loss of Fe^{3+} above pH 2 occurs when 20 mM Fe^{3+} is injected in a solution similar to the formation water at Sleipner field in the North Sea (Gauss et al., 2005) according to a preliminary speciation calculation using chemical equilibrium modelling software MINEQL+ 5.0 (Figure 2). At pH 7.7, which is the pH of formation water at Sleipner field, hematite precipitates as the solution becomes supersaturated with hematite. We did not consider any redox effect in these calculations. Our preliminary calculation shows that for concentrations ranging 0.2 mM to 20 mM, there is no stable aqueous Fe^{3+} above pH 3. Furthermore, additional loss of electrolyte takes place via hydrolysis of Fe^{3+} forming insoluble $Fe(OH)_3$, and via adsorption of Fe^{3+} onto mineral surfaces. Therefore, the stability of aqueous Fe^{3+} poses an additional problem that needs further investigation.

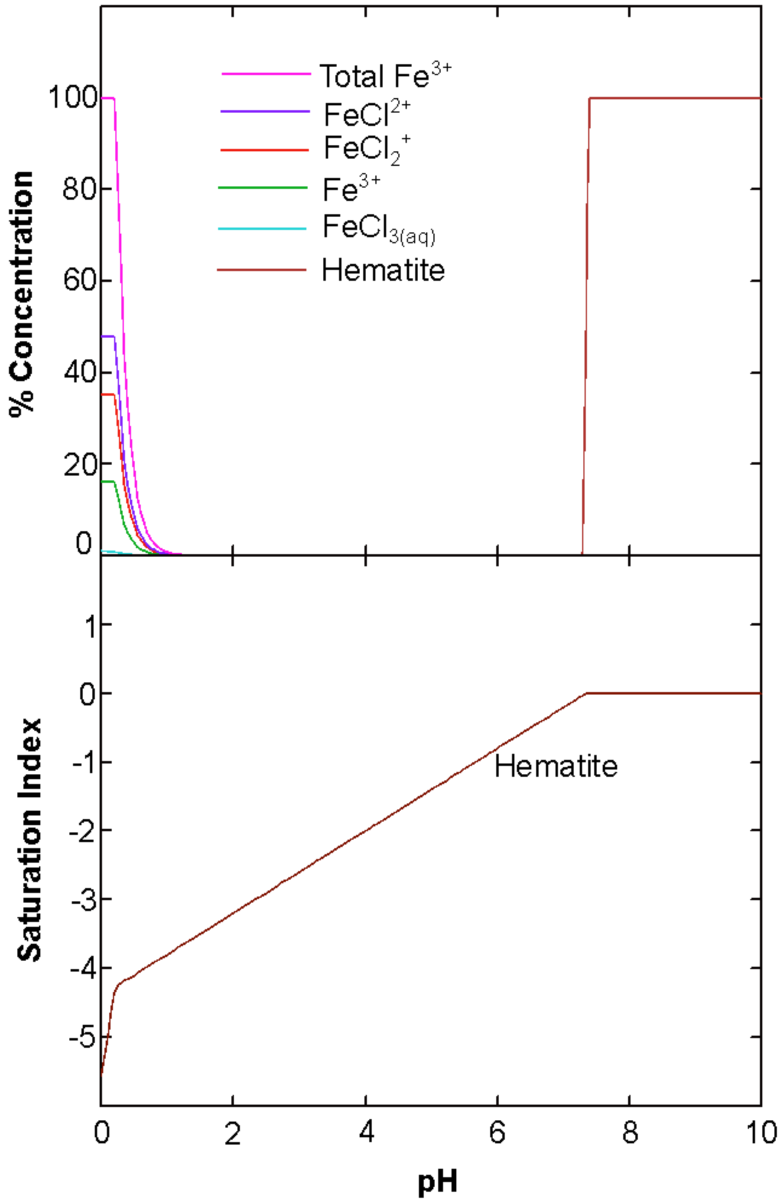

Figure 2. The top panel shows the the aqueous speciation of Fe^{3+} phases in a solution similar to formation water at Sleipner field, North Sea. The concentration of Fe^{3+} is 20 mM or 0.02 M. The solution contains 3.5×10^{-8} M Al, 1.25×10^{-5} M Ba, 0.177 M Ca, 0.479 M Cl, 2.48×10^{-7} M Fe^{2+}, 1.4×10^{-4} M K^+, 0.011 M Mg^{2+}, 0.1 M Na^+, 4.5×10^{-4} M Si, and 2.5×10^{-4} M sulphate. The bottom panel shows the saturation index of hematite with pH.

Microbes can also alter the electrolyte chemistry. In particular, charged electrolyte contains energy and is therefore a potential food-source (c.f. microbial contamination of stored H_2 (Zivar *et al.* 2021)). For example, in the presence of carbon compounds many anaerobic microbial communities “feed” by converting Fe(III) to Fe(II) (Chapelle 2001). Particularly, it has been shown that naturally occurring strains of sulphur oxidising microbes can reduce aqueous $FeCl_3$ under acidic conditions (Brock and Gustafson, 1976). This would short-circuit reaction (1). In other words, SFBs may suffer from microbially mediated self-discharge which could substantially reduce the useful storage duration and round-trip efficiency. Experiments are needed to quantify the severity of this problem as well as the extent to which it will be ameliorated by the moderately high temperature and salinity of the electrolytes. Experiments can also be undertaken to assess the effectiveness of “cleaning” the reservoir to remove carbon compounds.

A final consequence of bringing concentrated electrolytes into contact with natural brines is that it will lead to dilution through diffusive loss of ions. This will result in additional self-discharge and will require the electrolytes to be repeatedly “topped up”, adding further costs. Precipitates at the brine/electrolyte interface may help prevent this problem and numerical modelling will allow its severity to be evaluated.

If electrolyte contamination and dilution are resistant to the solutions suggested above, they may instead be ameliorated by pre-flooding the reservoir with a non-reactive gas so that electrolytes are no longer in direct contact with native brine (Fig. 3). An exciting possibility would be to use CO_2 as this barrier, since SFBs could then also play a role in carbon-sequestration. The presence of CO2 would also lower the pH and, hence, help to suppress the generation of precipitates discussed above. However, using a barrier gas would require the reservoir to be sealed above as well as below and this would reduce the number of suitable locations.

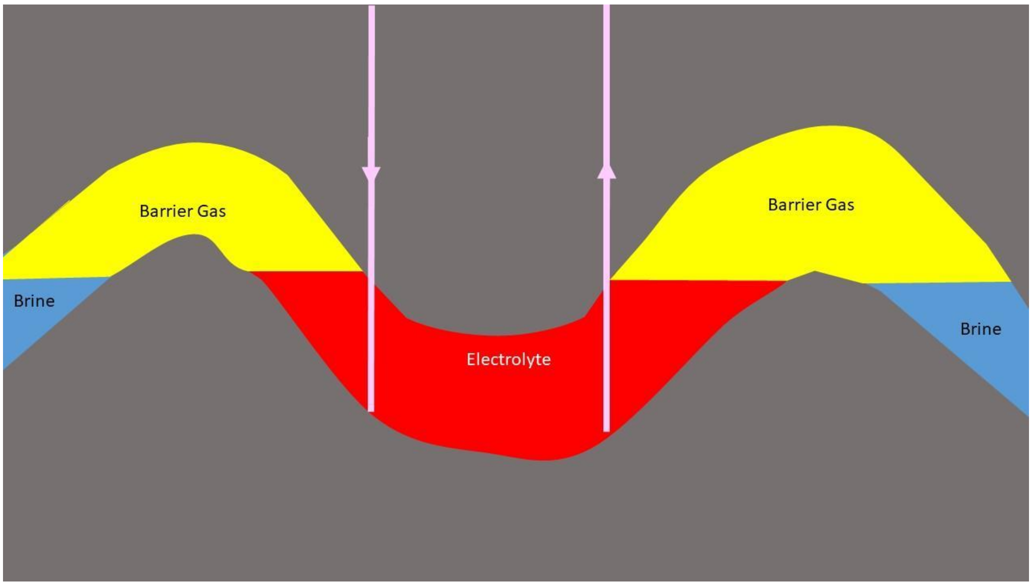

Figure 3. Protecting the electrolyte from contamination and diffusive ion-loss using a barrier gas (e.g. CO_2, N_2 or naturally present CH_4).

The fact that we plan to store electrolytes in porous media, rather than in well-mixed tanks, will also lead to novel problems. During charging we pump uncharged electrolyte out of one well whilst pumping-in charged electrolyte at another, spatially separate, well. The opposite happens during discharging (i.e. we reverse pumping direction so that discharged electrolyte is pumped into the uncharged electrolyte end of the reservoir). As a consequence, charged and discharged electrolytes are kept separate rather than being well mixed. Even after long-term use, there are likely to be significant ion-concentration gradients within the reservoirs. The consequences of this for flow-battery performance are unclear (it may even help!) but laboratory experiments are needed to investigate further. We therefore propose to set up a laboratory all-iron cell with 4 tanks—one for charged analyte, one for discharged analyte, one for charged catalyte and one for discharged catalyte—to determine how this separation affects performance.

Porous media additionally lead to the possibility that pore-spaces could become blocked by precipitates. This was mentioned earlier in the context of chemical contamination but precipitates can form even if there are no unwanted side-reactions since the iron deposited in reversed reaction (2) may not all be deposited on the electrode whilst the $FeCl_3$ involved in reaction (1) is a relatively low-solubility compound unless we operate the electrolyte at very low pH. Once again, laboratory work is required to evaluate the severity of these problems and to investigate possible solutions (e.g. additives and filters).

Furthermore, porous-rock storage leads to flow-rates (and hence power) being strongly constrained by electrolyte viscosity. The earlier calculations assumed that the electrolytes were sufficiently dilute that viscosity approximately equalled that of water. However, Yu *et al.* (2021) showed that the higher concentrations (2.2M) needed for good power (with iron sulphate electrolytes) led to a factor of 3 increase in viscosity. If a similar viscosity increase occurs in all-iron electrolytes too then it will reduce the power (but not the energy capacity) of the SFB by a factor of 3. Hence, we will need to determine the optimum compromise between energy density and viscosity when determining electrolyte concentrations. This requires further laboratory measurements.

A final set of problems, arising from sub-surface storage, is that the flow modelling of section 2 is highly simplistic and needs to be replaced with more realistic approaches. Sophisticated numerical models can investigate issues such as flow channelling (when flow becomes largely confined to a few, high permeability routes) and electrolyte trapping in cul-de-sacs (when electrolyte goes into an area but doesn't come out again). Both of these problems are well understood in the context of water-flooding of oil-fields to enhance recovery (e.g. Goudarzi et al. (2016)) and we anticipate that existing reservoir-modelling software will be able to investigate and evaluate the severity and impact of these problems.

We finish this section on potential problems with the need to obtain and retain public support. Given the oil industry's PR problems with hydraulic fracturing (Dodge and Metze 2017) and the fact that even wind-farms can be controversial (Ellis *et al.* 2007), it is likely that subsurface flow-batteries will meet resistance despite safety and environmental benefits. It is therefore necessary to discuss the technology openly and as widely as possible from an early stage. Issues that may affect acceptability relate to hydraulic fracturing, induced seismicity and contamination of ground water. Initial development in offshore settings may help mitigate public concerns.

A First Look at Cost

Sub-surface flow batteries look promising. They can potentially provide high charge/discharge power for weeks to months and none of the technical challenges appear insurmountable. However, it is also important to consider whether the technology is affordable.

Unfortunately, we have neither the space nor the expertise for a full economic assessment and, in any case, at this stage of development there are a great many uncertainties concerning the likely costs. For example, if highly acidic electrolytes are required, to combat the problem of precipitates, this will increase the costs of materials as they will need to be corrosion resistant. Given these uncertainties, in this section we simply attempt an order of magnitude look at costs in order to see whether sub-surface flow batteries are clearly so expensive that we can immediately rule them out.

We will consider two important cost-metrics: (i) the energy installation cost; (ii) the power installation cost (IRENA, 2017). The first of these is usually given in \$/kWh and expresses the price of a given amount of storage capacity. It allows direct comparison to the storage costs of alternatives (e.g. Li-ion batteries have an energy cost of \$200/kWh to \$1260/kWh whilst CAES is around \$53/kWh (IRENA, 2017)). The second metric is usually given in \$/MW and expresses the price for a given charge/discharge power. This is particularly useful for comparing to generating (as well as alternate storage) costs. For example, wind-turbines currently cost around \$1-2 million/MW and, ideally, we need storage power-costs to be significantly smaller than this so that adding storage does not greatly increase the overall cost of wind-turbine power.

To calculate these metrics, we start by estimating the capital cost of building the 736 MW, 249 GWh SFB discussed in section 2. Only an order-of-magnitude estimate is possible at this point and we do this by separating the costs into the flow-battery infrastructure cost plus the electrolyte cost. We start with the flow-battery infrastructure.

No flow-battery has ever been built on this scale or incorporating subsurface storage and so any estimate is, inevitably, crude. However, as already discussed, the installation is comparable in scale to that of an offshore oil production rig and the technology required is similar (i.e. largely involving pumping of fluids). In addition, a similar number and depth of wells will be required. Hence, a first estimate for the infrastructure costs can be given by the cost of a large production-rig plus wells. Average such costs are of the order of \$600 million (Investopedia 2021). This is undoubtedly a very crude estimate but it suffices for the purposes used below.

Electrolyte costs can be estimated much more firmly. Assume we start with 10^6 m^3 (from eqn. (17)) of 1 molar $FeCl_3$ (e.g. see optimum concentrations in Tucker et al, 2015), i.e. 10^9 moles of $FeCl_3$. This is 1.62×10^8 kg which, at a current industrial cost of \$0.5/kg (Alibaba 2021) is about \$80 million. Both electrolytes can be formed from $FeCl_3$ and, hence, total electrolyte feedstock cost is ~\$160 million to give an infrastructure+electrolyte cost of \$760 million. However, this is such a crude estimate that we are only confident in using it to give an order of magnitude. Hence, we estimate that the capital cost of our SFB will be of the order of \$1 billion.

The expected energy (249 GWh) and power (736 MW) then give an energy installation cost of roughly \$4/kWh and a power installation cost of around \$1 million/MW. Clearly, these are very crude estimates but they do allow a first-pass evaluation of the economics of SFB storage. In particular, the energy installation cost is extremely low (~10% of pumped hydro and ~1% of Li-Ion costs) whilst the power installation cost is competitive (similar to \$0.55-2.55 million/MW for pumped hydro power storage (Deane *et al.* 2010)).

These cost estimates finally bring us to the reason for choosing a well separation of 300m (i.e a=150m) in the preceding analysis. Larger well separations have the advantage that they increase the storage capacity and bring the energy installation cost down, but the energy installation cost is not an issue (it's already very low). The power installation cost, on the other hand, is badly affected by large well-separations since this reduces the power (due to lower flow rates) and increases the cost (due to higher capacity and, hence, more electrolyte). Smaller separations are therefore economically advantageous provided the energy capacity is sufficient for any particular application.

Conclusion

The first-approximation assessments made in this paper suggest that subsurface flow batteries may be able to provide safe multi-week electrical storage at high-power and low-cost. This concept therefore warrants further investigation.

Author contributions

DW: Conceptualization (equal), formal analysis (lead), methodology (equal), original draft (lead), review and editing (equal), project administration (lead); **KH**: conceptualization (equal), methodology (equal), review and editing (equal); **AB**: conceptualization (equal), methodology (equal), review and editing (equal); **SK**: conceptualization (equal), methodology (equal), review and editing (equal); **NL**: formal analysis (supporting), review and editing (equal).

Data Availability Statement

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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