Review of: "Flow Batteries From 1879 To 2022 And Beyond"

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Potential competing interests: No potential competing interests to declare.

First of, I would like to salute the significant effort that went into the literature review, patent search, and self-calculation of battery characteristics from available parameters. As an amateur of history of science myself, I thoroughly enjoyed the though process that went into underlining how progress in flow batteries evolved over time.
Too many literature reviews nowadays read like a bucket list of papers in the field, without much work being put in illustrating the evolution of the field.

I may have a few remarks on the paper however, which I will order in two categories, “minor” and “major” remarks:

I) Minor remarks

This section will focus on the ease of reading of the paper, figures and possible typos.

Blurry figures and equations

Fig.1 does not appear at all, Fig.2 and 3 are low definition, and Fig.4 is extremely small and low definition, which prevents me from reading the data presented. This may be due to the uploading process. Fig.7 and 8 on the other hand appear in high definition, maybe due to a different image format? Fig. 11A does not appear at all on the pdf but is clear on the web version, Fig. 11B is blurry on both. Parts of equations appear blurry on my screen in the pdf version, are they images?

Formatting bugs

E.g. on page 13, one paragraph has a weird alignment (the one with fiber sizes) on the pdf version. The alignment of equations (especially in the appendices) is not consistent.

Typos

Page 29 “pressure drop in the porous electrodes in acceptable” should be “is acceptable” “interdigitates” should be “interdigitated”. On page 37 Fig. I1 appears twice, I guess the second is Fig.I2

These remarks aside, the paper is generally well-written and pleasant to read. I also appreciated the sensible comparison between RFBs and LIBs towards the end.

II) Major remarks

This remarks will focus on the author calculations and conclusions.

I first have some interrogations about different definitions of efficiency:

Page 9: "80% round-trip energy (i.e. accounting for both voltaic and coulombic losses)" I would advise for the use of “energy efficiency” rather than “round-trip efficiency” as the latter tends to also account for the energy spent in pumping the fluid (and sometimes the BMS). Energy efficiency, on the other hand, is classically defined as Voltaic x Coulombic efficiencies.

To summarize:

- Round-trip efficiency is typically defined as (energy recovered during discharge) / (energy spent during charge). This accounts for all losses, including pumping and sometimes BMS.
- The voltaic efficiency is typically defined as (integral of the voltage over time during discharge) / (integral of the voltage over time during charge). This mostly accounts for ohmic losses and mass transfer limitations.
- The Coulombic efficiency is typically defined as (discharge capacity) / (charge capacity). This mostly accounts for side reactions and co-ions transport.

Reminding these definitions, or providing alternate ones, could be useful.

Page 10: “round trip voltage efficiency of 75%” similarly to above, voltage efficiency and round-trip efficiency refer to different things, so I would advise for consistency with literature nomenclature.

Page 12: I don't understand the black line on Fig.10 : the legend says “round-trip voltage efficiency” but the x-axis is also a “round-trip voltage efficiency” ?

Page 15: “In an actual VRFB application for a solar peak shifting, one can envisage a situation, where the charge takes a longer time during the day, but discharge takes a shorter time during the evening. Operating the system at 233 mA/cm2 during the charge and 573 mAcm2 during the discharge would result in approximately 80% ×71%= 57% round-trip efficiency”.

I am not sure about the multiplication of efficiencies here?

Talking about “one-way efficiency” is somewhat confusing without a proper definition and calculation in the preceding sections. If the value 80% refers to a Voltaic efficiency over a complete cycle (as is usually the case in the literature, i.e (integral of the voltage during discharge) / (integral of the voltage during charge)) than I suspect there might be a problem in the calculation.

It might be that the efficiency the author wants to calculate is actually an average of the two values provided (but again, it's hard to say for sure without proper definitions). It would also seems more coherent with the values provided on Fig.10, at a glance.

I somewhat struggle to see the link between section 3, Appendix D, and some of the author's conclusion:

First off, for reviewing calculations, it would be nice to have a table with different parameters that the author considered in his calculations, as well as an illustration of these parameters on a redox-flow cell scheme (e.g. a complete figure D1 with more parameters illustrated).

The quantity Delta P, is introduced as the pressure drop across the electrode between inlet and outlet, is imposed as 1 bar. The importance to keep this quantity the same on both sides of the membrane is underlined by the author, and drives a few of the calculations in this section: "In order to minimize the pressure difference across the membrane (and the resulting hydrodynamic flow) […]".

As far as I am aware of, typical pressure differences in reverse osmosis involve 5+ bars to get a significant flow. Plus, in a flow battery, the pressures at the outlet will be roughly equal to the atmospheric pressure. The pressure difference across the membrane would really only occur at the inlet, so that the pressure difference would need to be huge to lead to a significant flow.

We usually care more about osmosis and electro-osmosis, as far as I am aware of.

Page 13:

"Let's examine the predictions of Fig. 10. If we want to have for a VRFB battery's voltage round trip efficiency of 0.75, we see, that it can be obtained with the 0.46 μm diameter fibers in the negode and 0.71 μm diameter fibers in the posode, and the suitable discharge current density is 1.276 A/cm2. If we want to increase the voltage efficiency to 0.85, we need to reduce fiber diameters to 0.38 and 0.58 μm for the negode and posode, respectively. Also, the operating current density would need to be lowered to 0.857 A/cm2 (unless we are willing to increase pressure drop in the electrodes). This example shows, that decreasing fiber diameter in the porous electrodes of flow batteries can improve simultaneously two contradictory performance metrics: the area-specific power and the electric energy efficiency"

I don't think these two performance metrics are contradictory. If you decrease ohmic losses or mass-transfer limitations (which is probably what you're doing by decreasing the pore size) the discharge voltage is closer to its OCV value, so both the power density and the voltaic efficiency are increased.

What you're doing by decreasing the pore size, on the other hand, is that you're probably making it harder to reach high velocities in the electrodes, so you're probably having to spend more in pumping power. I am therefore surprised that "We shall clarify now, that we do not account for pumping energy losses in our analysis for two reasons" on page 12. The actual round-trip efficiency (as in the literature definition of "energy recovered during discharge" / "energy spent during charge") accounts for pumping losses, and the trade-off faced by flow battery operators is usually that increases in voltaic efficiency may result in increases in pumping losses, so that the round-trip efficiency may overall decrease by using thinner electrode fibers. I am surprised to see many considerations on kinetic factors in Appendix A-B-C, but very few on hydraulic ones such as fluid viscosity (which is not defined in Appendix C but should be the parameter nu in the Darcy equation), flow rate and pumping power. This is where I would expect the trade-off to be, and not between power density and voltage efficiency.

Misunderstandings in efficiency may lead to questionable assessments in Section 4 “The “lithium or vanadium” quandary”

I command the initiative of the author to provide a techno-economic assessment of both technologies, but I disagree with a few points made in this section:

1. Capital cost is important, but it is a bit of chicken and egg problem: if many people invest in the technology, capital cost goes down through learning curve effects. If not, it doesn't. Assessing the viability of Lithium-ion with 2005 data is probably pretty bad, but a lot of people still invested back then, and the costs went down.
   I believe a proper cost analysis would first compare other parameters (such as electricity prices, efficiency and lifetime) to identify revenue streams where flow batteries can compete on the long term (disregarding CAPEX), and account for a learning curve effect to assess whether the required drops in CAPEX to make the technology viable are realistic or not.
2. Energy/Power ratio (i.e. storage time): I think modern Li-ion systems can go up to 4h of discharge at peak rated power.
3. Durability: the main argument for Vanadium is that the capacity is recoverable by rebalancing the electrolytes, which are very durable. Some companies even lease vanadium electrolytes to flow battery operators. The modularity of the battery generally allows for more maintenance possibilities, but it adds in OPEX.
4. Round-trip efficiency (and not energy efficiency): I did not see mentioned these two phenomena:

- Shunt currents: due to the high conductivity of flow battery electrolytes, some amount of current goes through the piping system rather than the membrane, leading to some losses
- Pumping losses: fluid viscosity, electrode permeability and design of the piping system lead to losses compared to static batteries such as LIBs.

Those are, to my knowledge, contributing to the lower round-trip efficiency of flow batteries. To which we could add the ohmic resistance of the felt and the membrane, which contribute to a lower energy efficiency.

I agree with the following points, numbered 1-16 on page 18 and 19, but not necessarily on the conclusions with respect to future markets for RFBs.

This is how I would have conducted this section:

I will illustrate what I think with a hypothetical day-ahead market, where electricity prices are 0 between 10pm and 10am, and $100/MWh between 10am and 10pm.

The ideal storage duration in this market is obviously 12h. A 1MW/4MWh Li-ion battery would only be able to charge for 4h when electricity is free, and bring a revenue of $400 when electricity is expensive. A flow battery rated at 1MW/12MWh would be able to charge for free during 12h, and bring a profit of $1200 during discharge.

Now, I assumed a 100% efficiency, but we can see that even if the flow battery is less efficient, it can still compete due to its larger capacity.

Finally, the CAPEX of the flow battery is probably higher, but we can calculate how long it would take to pay for itself, compared to the LIB. And we can then compare this value with their respective lifetime.

I think what matters the most is not the price of input electricity, but the differential in prices between charge and discharge, and how they reward power vs. energy (e.g. frequency reserve markets and day-ahead market).

My general conclusion on the paper is that I would probably have split in two: section 1, 2 and 4 make for a good review paper, and section 3 + Appendices would make for an interesting modelling paper, although my points above should be adressed.