

4th Annual CDT Conference in Energy Storage and Its Applications, Professor Andrew Cruden,
2019, 07-19, University of Southampton, U.K.

The use of gold impregnated carbon-polymer electrodes with the soluble lead flow battery

Ewan J. Fraser^{*}, Richard G.A. Wills, Andrew J. Cruden

Energy Technology, Faculty of Engineering and Physical Sciences, University of Southampton, SO17 1BJ, UK

Received 12 February 2020; accepted 25 February 2020

Abstract

The soluble lead flow battery (SLFB) is a hybrid redox flow battery. During charge, lead and lead dioxide are deposited onto the negative and positive electrode surfaces respectively from Pb^{2+} ions dissolved in a methanesulfonic acid electrolyte. Many of the challenges for the SLFB are related to these solid deposits, particularly the positive lead dioxide deposit. Gold has been shown to be an effective substrate for lead dioxide deposition. However, the prohibitively high cost of pure gold prevents its use as an electrode material. Therefore, using low mass loadings of gold at the surface of carbon-polymer electrodes is proposed. Gold impregnated carbon-polymer electrodes are tested in static electrolyte soluble lead cells. The addition of gold leaf onto the surface of the electrodes improved the peak energy efficiency by 5%. The cycle life of the cell was also improved from 13 cycles using plain electrodes to 29 cycles using the gold plated electrodes. The use of gold at the positive electrode appears to reduce the likelihood of failure due to shorting.

© 2020 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the scientific committee of the 4th Annual CDT Conference in Energy Storage and Its Applications, Professor Andrew Cruden, 2019.

Keywords: Soluble lead; Gold; Redox flow battery; Electrode additive; Lead dioxide; Lead

1. Introduction

Redox flow batteries (RFBs) are electrochemical storage devices that are able to provide energy at high power for a long duration. The soluble lead flow battery (SLFB) is one type of RFB [1]. The SLFB differs from conventional RFBs in that solid lead and lead dioxide are deposited at the negative and positive electrodes respectively. Both half-reactions in the SLFB use the Pb^{2+} species. The combination of these two aspects allows the SLFB to operate in an undivided manner.

However, the thickness of solid deposits that form in the SLFB is limited and hence in the amount of energy it can store for a given electrode area. Thick deposits are, therefore, advantageous.

In order to ensure thick deposits are possible, the interface between the electrode and the deposit must be considered. Typically, two-dimensional, planar, bipolar carbon-polymer electrodes are used with the SLFB. One method of ensuring thick deposits is to use a three-dimensional electrode, thus increasing the effective electrode

^{*} Corresponding author.

E-mail address: ef5g12@soton.ac.uk (E.J. Fraser).

<https://doi.org/10.1016/j.egy.2020.02.023>

2352-4847/© 2020 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the scientific committee of the 4th Annual CDT Conference in Energy Storage and Its Applications, Professor Andrew Cruden, 2019.

area. Oury et al. have produced a cell with a honeycomb-shaped positive electrode to such an effect [2]. Reticulated vitreous carbon (RVC) has also been used as a three-dimensional electrode for the SLFB [3–7].

Another method is to use improved electrode materials. Nickel electrodes have been used for the SLFB in several studies, most commonly as the negative electrode [6–10]. Copper electrodes have also been used as a negative electrode [2]. Rough lead deposits formed at the copper electrodes despite the addition of a smoothing additive hexadecyltrimethylammonium hydroxide (HDTMA). However, the electrode material was not the focus of this study.

In this work, gold is used as the surface layer of the electrode. Gold is prohibitively expensive to use as the bipolar plate or in high mass loadings in the electrode. Therefore, small quantities of gold are used at the surface of the electrodes.

2. Experimental

An electrolyte consisting of 1 M methanesulfonic acid, 0.7 M lead methanesulfonate, 1 g dm⁻³ sodium lignosulfonate and 2.5 mM bismuth (III) oxide dissolved in deionized water was produced. The cells used in all experiments were static electrolyte cells, i.e. only the volume of electrolyte between the electrodes was occupied by electrolyte and this electrolyte was not circulated or stirred. The cell frames were cut out from 3 mm thick acrylic sheet. Two of these sheets were stacked and, along with the electrodes, were sealed using a silicone sealant. The cells had an active area of 25 cm². The carbon-polymer plates used are SGL SIGRACELL® PV15 bipolar plates. Copper current collectors were used at both sides of the cells. Each cell was clamped using steel endplates insulated from the current collectors using a 1.5 mm sheet of acrylic.

The cells were cycled using an MTI 8-channel battery analyser. The cells were charged and discharged at an equal, constant current. Each cycle consisted of a charge, a 10 min rest, a discharge and a further 10 min rest. A discharge cut-off voltage of 0.3 V was used.

Gold leaf plated electrodes were manufactured using the commercial PV15 bipolar plates as a base. A 5 cm × 5 cm square of 23ct (95.83% pure) gold leaf was placed in the centre of a 7 cm × 7 cm square of PV15. The electrode was then placed in an aluminium mould to ensure minimal deformation of the electrode. The mould was then heated using an MTI hot press set to 250 °C for a minimum of 15 min. A force of 20 kN was then applied to the electrode for 30 s. Finally, the electrodes were left to cool to ambient temperature before removal from the mould.

3. Results and discussion

3.1. Cell efficiencies

A single cell with plain carbon-polymer electrodes and a cell with gold-leaf plated electrodes were cycled at a current density of 10 mA cm⁻². The cells were charged for 15 min and discharged to a cut-off voltage of 0.3 V. Fig. 1(a) shows the coulombic, voltage and energy efficiency of each cycle. All of the efficiencies are low in cycle

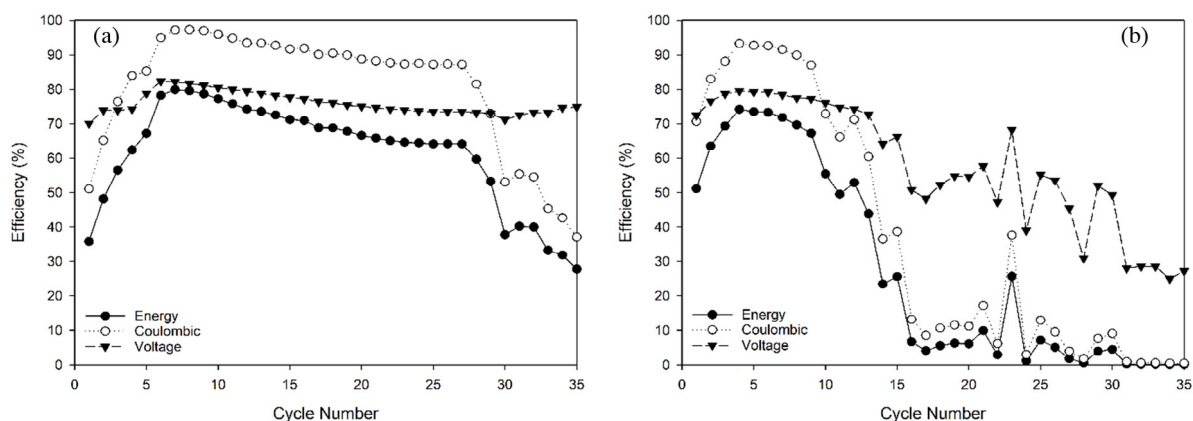


Fig. 1. Charge, voltage and energy efficiencies for each cycle of a cell using gold leaf plated carbon-polymer electrodes, (a), and a cell using plain carbon-polymer electrodes, (b). Both cells were charged at 10 mA cm⁻² for 15 min and discharged to 0.3 V.

1, at 70.1%, 51.1% and 35.8% for the voltage, coulombic and energy efficiencies respectively. All three efficiencies rise over the subsequent 5–7 cycles, peaking at 82.3% in cycle 6, 97.3% in cycle 8 and 79.93% in cycle 7 for the voltage, coulombic and energy efficiency respectively. The efficiencies steadily decrease until cycle 27, after which point the coulombic efficiency and hence the energy efficiency decrease more rapidly. The cell is deemed to have failed when the coulombic efficiency drops below 60% in the 30th cycle.

A similar trend is seen in the results from the plain carbon-polymer electrodes, described in Fig. 1(b). The coulombic efficiency and hence the energy efficiency in cycle 1 are higher but voltage efficiency was comparable to that seen in the cell with gold leaf plated electrodes with coulombic, voltage and energy efficiencies of 70.7%, 72.4% and 51.2% respectively. However, the efficiency peaks earlier, in cycle 4 and at marginally lower values of 93.3%, 79.5% and 74.2% for the coulombic, voltage and energy efficiencies respectively. The lower efficiencies witnessed during the first few cycles are visible when additives are used [11]. However, this is exacerbated when gold electrodes are used. This could be due to a greater resistance to stripping of the initial deposits at one or both of the electrodes. Alternatively, it may be due to a reduced affinity for deposition due to the additives in the electrolyte and by the gold on the electrodes. The efficiencies decrease steadily, until the 9th cycle when the efficiencies rapidly decrease. The cell is deemed to have failed by the 14th cycle.

Fig. 2 shows the charge voltage and energy efficiencies of cells with a single gold-coated electrode at the positive (a) and the negative (b) electrode respectively. The other electrode is a plain carbon-polymer electrode. Fig. 2(a) shows all three efficiencies are low in cycle 1 at 40.3%, 71.4% and 56.4% for the energy, voltage and coulombic efficiencies respectively. Again, the efficiencies rise, reaching a peak during cycle 8 at 73.7%, 78.9% and 93.4% respectively. The cell had failed by cycle 10, however. In Fig. 2(b), the efficiencies are again low in cycle 1 at 49.5%, 71.7% and 69.0% for energy, voltage and coulombic efficiencies respectively. In this cell, however, the efficiencies rose much quicker, reaching a plateau after cycle 3 at 70.7%, 78.7% and 89.9% respectively. The efficiencies remain relatively constant until cycle 17 when all three decrease rapidly. The cell has failed by cycle 19.

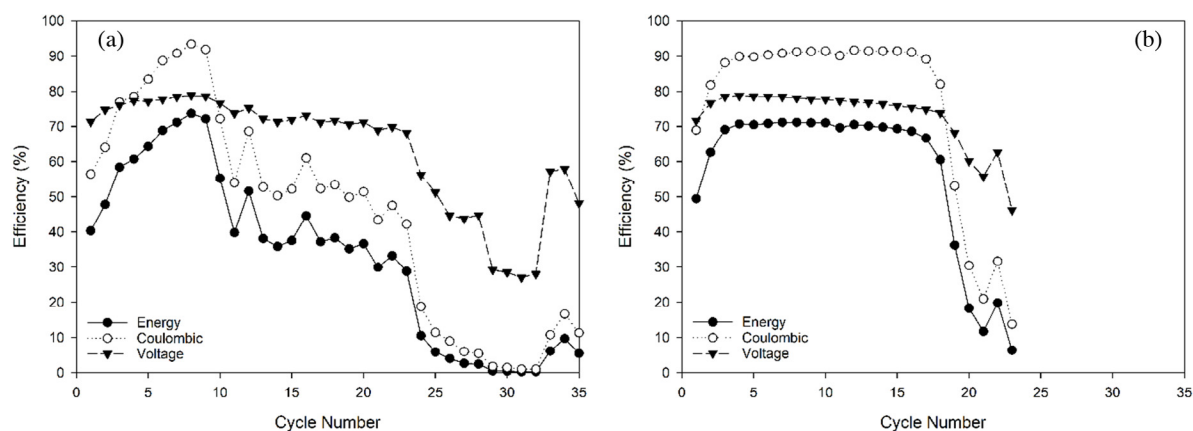


Fig. 2. Charge, voltage and energy efficiencies for each cycle of cell using gold leaf plated carbon-polymer electrodes at the positive electrode only (a), and at the negative electrode only, (b). Both cells were charged at 10 mA cm⁻² for 15 min and discharged to 0.3 V.

3.2. Cell failure

The mode of failure of each of the cells is also of interest. By comparing the cycle during which the voltage efficiency begins to decrease with the cycle during which the coulombic efficiency begins to decrease, it is possible to suggest if the cell failed due to shorting between the electrodes, such as due to a buildup of sludge from materials fallen from the electrode, or from another mode of failure, such as capacity fade due to the complex mechanisms at the positive electrode. The cells for which the voltage efficiency decreases at a similar time to the coulombic efficiency, the cell using plain carbon-polymer electrodes and the cell with gold at the negative electrode, suggest that the cell failed, at least partly, due to shorting. Cells for which the voltage efficiency remains high after failure, the cell with gold at both electrodes and the cell with gold at the positive electrode, suggests the cell failed due to another mechanism. The voltage curves of the cells shortly after failure, shown in Fig. 3, support this theory.

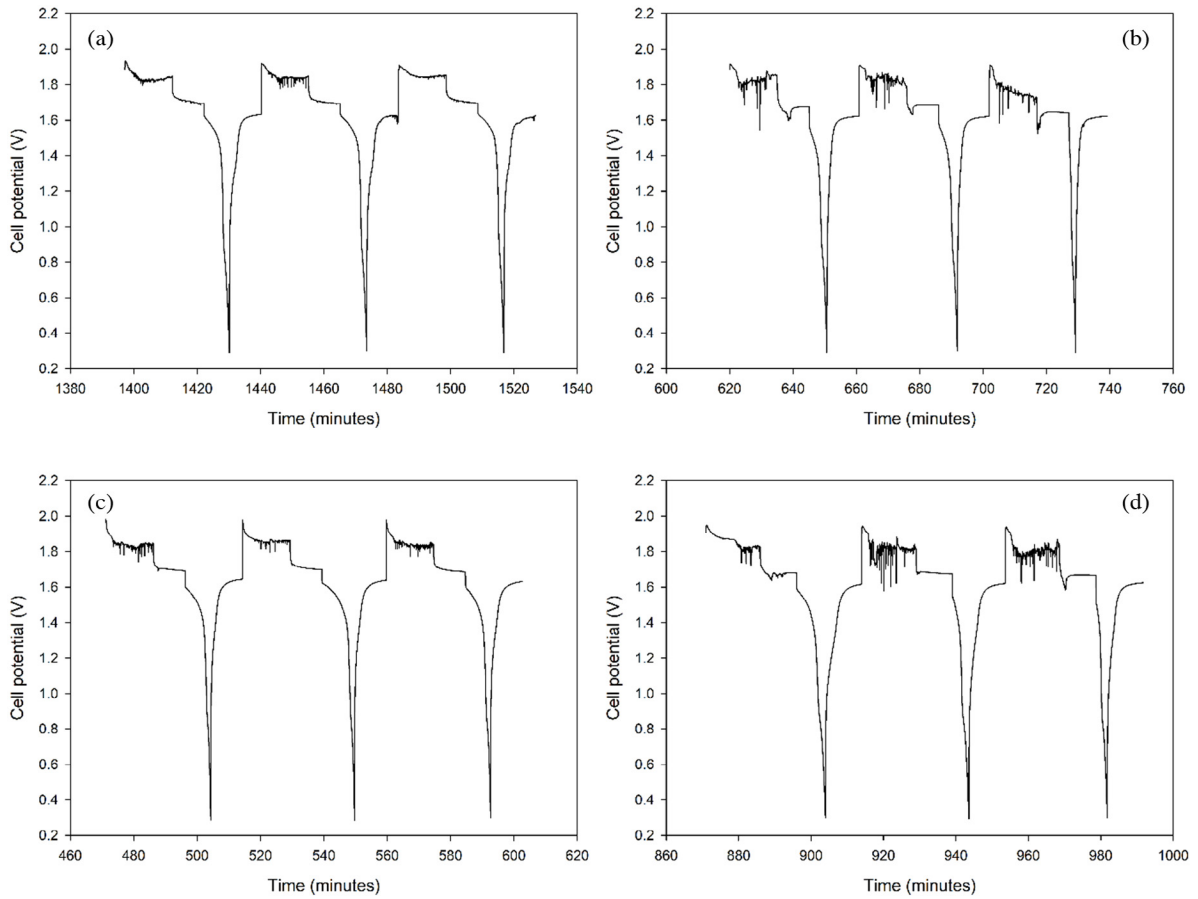


Fig. 3. Cell potential vs time for the three cycles post failure for: gold leaf on both electrodes (a), plain carbon-polymer electrodes (b), gold leaf on only the positive electrode (c), and gold leaf on only the negative electrode (d).

Fig. 3(a) and (c) (the cell with gold at both electrodes and the cell with gold at the positive electrode) show little noise in the voltage curve and so suggest that little shorting has occurred. Fig. 3(b) and (d) (the cell with plain carbon-polymer electrodes and the cell with gold at the negative electrode) show significantly more noise in the cell potential and hence suggest that there is some shorting of the cells. It is known that sludge can form from material at the positive electrode [6], which, in a static cell would gather at the bottom of the cell and cause a short circuit between the electrodes. This data suggests that gold may prevent, or hinder a buildup of this sludge at the positive electrode. However, further work is required to confirm this theory.

3.3. Economics

The obvious caveat to the use of gold as an additive to electrodes is the price. Using the raw material prices for materials commonly used to manufacture bipolar plate electrodes, gold leaf coating the entire surface of the electrode becomes the significant cost in manufacturing the electrode. Fig. 4 shows the proportion of the costs of components in a typical RFB cell. In this instance, the cell does not include the endplates, the electrolyte or any of the flow circuitry including the pump. The cell is assumed to be part of a stack, so each cell consists of a single bipolar plate (the stack is assumed to be large enough to ignore the extra electrode required at the end of the stack), a cell frame. Four cells are described: an undivided cell with plain electrodes, an undivided cell with gold plated electrodes, a divided cell with plain electrodes and a divided cell with gold plated electrodes. It is assumed that the gold is plated uniformly to a thickness of 0.1 μm on the active area of the electrodes. The separator is assumed

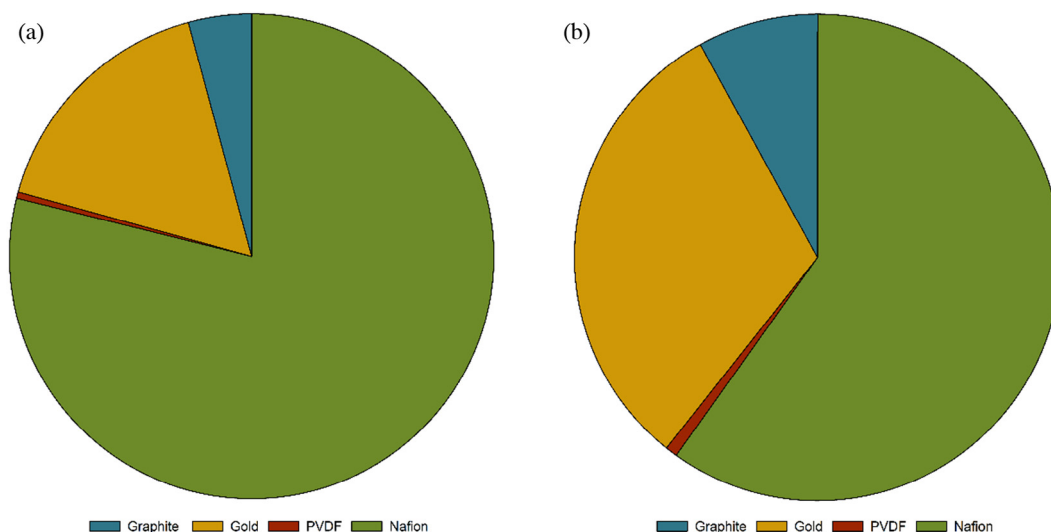


Fig. 4. Proportion of cell cost by material using current (a) and a future prediction (b) for the cost of Nafion.

to be a Nafion ion exchange membrane. The cell frame is not included due to the amount of material required depending heavily on the design of the flow field and physical form of the electrodes.

The costs of graphite and PVDF are approximately $\text{£}8 \text{ kg}^{-1}$ and $\text{£}5.50 \text{ kg}^{-1}$ respectively [12]. A plain carbon polymer consisting of graphite with a polyvinylidene difluoride (PVDF) binder, assumed to have a ratio of 85:15 respectively and to be 1 mm thick, would cost approximately $\text{£}20 \text{ m}^{-2}$. The addition of $0.1 \text{ }\mu\text{m}$ of gold, the thickness presented in this work, would add a further cost of approximately $\text{£}60 \text{ m}^{-2}$, a significant increase [13]. A Nafion membrane, however, would cost approximately $\text{£}300 \text{ m}^{-2}$, potentially reducing to $\text{£}120 \text{ m}^{-2}$ in the future [14]. As the SLFB is able to operate without a membrane, the addition of gold may, therefore, be feasible. Furthermore, gold may be beneficial in much lower mass loadings than represented here. Further work is, however, required.

4. Conclusions

These preliminary results show that the use of gold in electrodes for the soluble lead flow battery has promise. When gold is used at both electrodes there is a significant increase in performance. The cycle life is doubled and there are increases in both coulombic and voltage efficiencies. These results were gathered from cells with a static electrolyte at relatively low currents. While this is assumed to be indicative of performance in a flow cell, testing on flow cells over a greater period at higher currents is necessary.

The mode of failure when gold is not present appears to be a mode other than shorting. It can be concluded that the addition of gold to the positive electrode may reduce the likelihood of shorting, probably due to a reduced volume of sludge forming at the positive electrode when gold is present. However, further work is required to confirm this theory.

Furthermore, the cost of gold in the mass loadings used is significant but not excessive when compared to other components in a flow cell. Further techniques to improve the addition of gold to electrodes and varying the mass loading of gold on the surface of these electrodes is also necessary. Further analysis of the deposits formed on these gold impregnated electrodes would also be beneficial.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank James Le Houx for his enlightening discussion and useful comments. The authors would further like to acknowledge the financial support received from the Engineering and Physical Sciences Research Council (EPSRC) through the Centre for Doctoral Training in Energy Storage and its Applications grant EP/L016818/1.

References

- [1] Krishna M, Fraser EJ, Wills RGA, Walsh FC. Developments in soluble lead flow batteries and remaining challenges: An illustrated review. *J Energy Storage* 2018a;15:69–90.
- [2] Oury A, Kirchev A, Bultel Y. Cycling of soluble lead flow cells comprising a honeycomb-shaped positive electrode. *J Power Sources* 2014;264:22–9.
- [3] Czerwiński A, Zelazowska M. Electrochemical behavior of lead dioxide deposited on reticulated vitreous carbon (RVC). *J Power Sources* 1997;64:29–34.
- [4] Czerwiński A, Zelazowska M. Electrochemical behavior of lead deposited on reticulated vitreous carbon. *J Electroanal Soc* 1996;410:55–60.
- [5] Banerjee A, Saha D, Row TNG, Shukla AK. A soluble-lead redox flow battery with corrugated graphite sheet and reticulated vitreous carbon as positive and negative current collectors. *Bull Mater Sci* 2013;36:163–70.
- [6] Wills RGA, Collins J, Stratton-Campbell D, Low CTJ, Pletcher D, Walsh F. Developments in the soluble lead–acid flow battery. *J Appl Electrochem* 2010;40:955–65.
- [7] Pletcher D, Wills R. A novel flow battery: A lead acid battery based on an electrolyte with soluble lead (II) Part II. Flow cell studies. *Phys Chem Chem Phys* 2004;6:1779–85.
- [8] Collins J, Kear G, Li X, Low CTJ, Pletcher D, Tangirala R, et al. A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II) Part VIII. The cycling of a 10 cm × 10 cm flow cell. *J Power Sources* 2010;195:1731–8.
- [9] Schlesinger M, Paunovic M. *Modern electroplating*. John Wiley & Sons; 2011.
- [10] Pletcher D, Zhou H, Kear G, Low CTJ, Walsh FC, Wills RGA. A novel flow battery: A lead–acid battery based on an electrolyte with soluble lead(II) Part V. Studies of the lead negative electrode. *J Power Sources* 2008;180:621–9.
- [11] Krishna M, Wills R, Shah A, Hall D, Collins J. The separator-divided soluble lead flow battery. *J Appl Electrochem* 2018b;48:1031–41.
- [12] Peters JF, Peña Cruz A, Weil M. Exploring the economic potential of sodium-ion batteries. *Batteries* 2019;5:10.
- [13] Bloomberg. Gold, British pound spot price. 2019.
- [14] Minke C, Turek T. Economics of vanadium redox flow battery membranes. *J Power Sources* 2015;286:247–57.