State of the art of all-Vanadium Redox Flow Battery: A Research Opportunities

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Abstract

This paper deals with the state of the art of redox flow battery (RFB) focusing on vanadium-based electrolytes. A broad review on energy storage technologies is first presented to bring RFBs system into perspective. Subsequently, discussions are focusing on vanadium-based RFB in regards to justify the motivation factors of chosen V-RFB as a system to be studied. Research potential and challenges for V-RFB system are discussed in detail.

Keywords: redox flow battery, all-vanadium redox flow batteries, energy storage, hybrid electric vehicle

1. Introduction

Over the last few years, many types of RFB have been considered; including bromide-polysulfide, vanadium-vanadium, vanadium-bromine, iron-chromium, zinc-bromine, zinc-cerium, and soluble lead RFBs. This paper anyhow would focusing on vanadium-based system as scope of the study while details review of the RFBs has been provided by Ponce et al. (Ponce-de-León et al., 2006). A concise summary of the energy storage technologies is first reviewed in intention of bringing V-RFB into perspectives. Research potential and challenges for V-RFB system are discussed.

2. Overview of Energy Storage Technologies

In general, the energy storage technology can be grouped in 3 main categories i.e. mechanical storage systems, electrical storage systems, and electrochemical storage system.

In mechanical storage system, while it has been installed for many applications, safety is the major obstacle for variety of applications. Flywheel technologies for example, even though it has been around for more than a century, this technology is only considered significant as energy storage for various applications due to the improvement in materials, magnetic bearing control and power electronics technologies (Hebner et al., 2002) in 1980s. Although it exhibits many advantages such as environmentally friendly, free from depth of discharge effects, could deliver high power and energy density, yet the system remains under review for larger commercial use due to safety of flywheel tensile strength that would cause wheel-flying apart. Further durability flywheel management and better storage is still in research to overcome the limitation.

Alternatively, in electrical storage system, despite the fact that it operates at very high efficiency, the high power density but lower energy density delimits its applications. Ultra-capacitor for instance, could deliver very high power density, rating at 10 – 100 s kW, but it could only deliver a very low energy capacity (< 1 kW h) (Chen et al., 2009). The same with superconducting magnetic energy storage (SMES), high cost and environmental issues associated with strong magnetic field are major concerns for technology development. Current technology rating at 1 – 10 MW for small SMES (storage time in seconds) whereas larger scale of SMES rating at 10 – 100 MW (storage time in minutes) (Koshizuka et al., 2003). Therefore, the system is not intended to replace the other energy storage, but rather complimenting in whole energy storage system (Blanc, 2009).

Electrochemical storage energy has become the oldest and most established energy storage devices which not only provide energy flexibility and environmental benefits, but also offer a number of important operating benefits to the load (Chen et al., 2009). It main advantages are ability to response for quick load demand, generally very high energy efficiency (average of 80 %) and simplicity for modularity (Kondoh et al., 2000). This has become very attractive features for various applications.

While conventional lead acid has matured and proven to be cheaper (~ $200 / kW h) and most reliable energy storage for many years, its applications has been delimited by short cycle life (around 1000 cycles), low energy density (50 W h kg^{-1}), limited depth of discharge and poor low temperature performance(Gonzalez et al., 2004). Nickel cadmium (NiCd) is other types of electrochemical energy storage that has matured and used in various applications; rating at 75 W h kg^{-1}. Nevertheless, NiCd suffers from memory effect phenomenon, high manufacturing cost ($1000/kW h) and disposal of toxidic-cadmium (Chen et al., 2009).

With a very high energy density of 200 W h kg^{-1}, lithium ion has captured most interest in recent years for various applications, including mobile electronic devices. Latest interest is for powering vehicle as sole power or hybrid system. Nevertheless, due to the limitation of temperature for the batteries to operate safely, the main hurdle for this system is high cost (> $600/kW h) for proper battery management system and protection circuit as well as special packaging (Gonzalez et al., 2004).

Fuel cells (FCs) are claimed to offer a promising alternative to conventional batteries (Cook, 2002; J. A. Smith et al., 2002; Pera et al., 2002; Pathak et al., 2006). FCs have the potential to provide a high efficiency while greatly reduced tailpipe emissions (Dhameja, 2002), in addition to fast refuelling. However, several technical issues must be addressed before FCs could become a realistic power source(Mohamed et al., 2009). The storage of hydrogen in compressed tanks is a particular concern; hydrogen gas requires pressures and temperatures in excess of 34 MPa and –253 ^{o}C, is a critical safety issue (Husain, 2003; J. Larminie et al., 2003; He et al., 2006; S. G. Chalk et al., 2006). In addition, the infrastructure needed for generation and transportation of hydrogen is virtually non-existent (Romm, 2004). High energy-cost per kW for effective hydrogen generation as well as expensive platinum catalyst makes fuel cell very expensive compared to other batteries.

Developed since 1970s (Fedkiw et al., 1984), RFB is a rechargeable electrochemical energy storage device, whereby system power and storage capacity can be largely decoupled, which the former is determined by the design of the cell stack and its size, while the size of the tanks, the amount of electrolyte and the concentration of reactant defines the latter. In concept, RFBs are similar to FCs, except that the electrolyte in FC system remains within the cell stack, whereas electrolyte in RFB flows through the cell stack to allow redox reaction takes place. Advantages of RFB system are as follows (Joerissen et al., 2004):

i. No self-discharge during storage period
ii. No solid state phase changes during charge-discharge
iii. The electrolyte has indefinite cycle life

Among others, vanadium-based RFB is one of promising electrochemical energy storage due to the cost of vanadium may be acceptable, as it is a relatively abundant material, which exists naturally in approximately 65 different minerals and fossil fuel deposits (Li et al., 2011). To date, compared to other types of RFB, vanadium-based are the most developed and the most close to commercialization (Skyllas-Kazacos et al., 2011). Table 1 summarises the comparison of selected energy storage.

3. Vanadium-based RFB

In contrast to other type of RFB, vanadium – vanadium RFB (also refers to all-vanadium RFB or V-RFB) uses same electrolyte species for both half – cells, thereby eliminating cross-contamination problem as experienced in bromide-polysulphide RFB resulting in simplification for electrolyte management. The electrolytes are prepared by dissolving vanadium pentoxide, V_2O_5 in sulfuric acid H_2SO_4 and use cationic exchange membrane to transport proton across it during redox reaction; where Nafion® 112 and 117 membranes were suggested to show a good stability for the system (Sukkar et al., 2004).

V-RFB is regarded as one of the few electrochemical energy storage systems suitable for many applications due to its high reported energy efficiency (>80%)(Skyllas-Kazacos et al., 1997; Skyllas-Kazacos, 2003). V-RFB offers several distinct advantages over other type of RFB and has been considered for various applications including for mobile application such as powering electric vehicle (Rychcik et al., 1988; Rahman et al., 2004). Figure 1 shows the structure diagram and principles of operation of V-RFB. The cell reactions are as follows:

Positive electrode:

$$VO^{2+} + H_2O \rightleftharpoons VO_2^{+} + 2H^{+} + e^{-} ; \quad E^{o} = 1.00 \text{ V } vs. \text{ SHE} \quad (1)$$

Negative electrode:

$$V^{3+} + e^{-} \rightleftharpoons V^{2+} ; \quad E^{o} = -0.26 \text{ V } vs. \text{ SHE} \quad (2)$$

Note : $VO^{2+} \cong V^{4+}$; $VO_2^{+} \cong V^{5+}$

Therefore, a novel vanadium chloride / polyhalide RFB has been proposed (Skyllas-Kazacos, 2003) by applying VCl_2/VCl_3 in the negative half-cell electrolyte and the $Br^-/ClBr_2^-$ couple in the positive half-cell. At 20 mA cm^{-2} current density 83 % and 80 % of coulombic and voltage efficiency respectively was recorded; slightly lower compared to V-RFB coulombic efficiency of 87 % achieved at 15 mA cm^{-2}. The system aimed to provide solution for V-RFB system for its low energy density but no further remark on this matter was found in literature. It was noted that the system has expected cell potential comparatively to V-RFB system of 1.3 V (Skyllas-Kazacos, 2003). Meanwhile, another vanadium / polyhalide was proposed which employed VBr_2/VBr_3 and was claimed possible to achieve energy density of 50 W h kg^{-1} VBr_2/VBr_3 (Ponce-de-León et al., 2006). No further cell performance was found in the literature for this system.

Table 1 Comparisons of selected energy storage technologies at different parameter (Gonzalez et al., 2004).

Types	Power rating	Discharge	Efficiency	Lifetime	Status	Issue
Pumped hydro	100- 4000 MW	4 - 12 h	85 %	30 years	Commercial	Exclusion area
Flywheels	< 750 kW	< 1 h	> 90 %	20 years	Prototype	Containment
Ultracapacitor	< 100 kW	< 1 min	95 %	10,000 cycles	Commercial	Short period
SMES	10- 10 MW	1 - 30 min	95 %	30 years	Design	Short period
Lead-acid	< 50 MW	1 min - 8 h	85 %	2 - 10 years	Commercial	Lead disposal
Li-ion	3 kW	1 min	> 95 %	10000 cycles	Commercial	Thermal runaway
V -RFB	< 3 MW	< 10 h	85 %	10 years	In test	Low energy density
PSB RFB	< 15 MW	< 20 h	75 %	2000 cycles	In test	Cross-contamination
FC	< 250 kW	as needed	40 %	10 - 20 years	In test	Safety

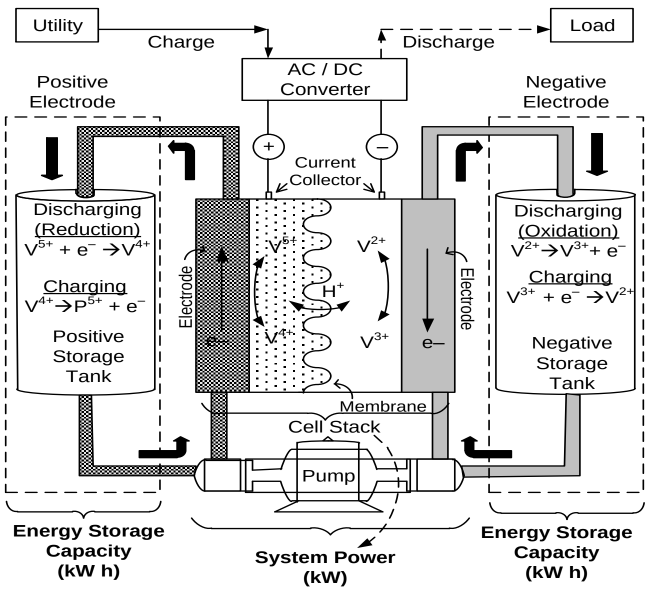

Figure 1. Single stack flow circuit to describe the principles of operation, main components of a V-RFB system, and parts to establish the power and energy rating of the system (adapted from (Mohamed et al., 2009))

Furthermore, Mn^{2+} / Mn^{3+} was proposed as electrolyte species for anolyte active species due to its higher standard potential i.e. 1.51 V compared to VO^{2+}/VO_2^+ of 1.00 V in V-RFB system (Tao et al., 2009). It was reported that for 1.2 mol dm^{-3} Mn^{2+} / Mn^{3+} system, 92.5 % coulombic efficiency, 93.5 % voltage efficiency and 40.8 W h kg^{-1} were recorded. The results show an attractive alternative of V-RFB system especially for mobile application, but disproportional reaction of Mn^{3+} producing MnO_2 on carbon felt reserved the application of VMn^{2+} / VMn^{3+} RFB (Tao et al., 2009).

Thus, judging from all redox flow battery systems especially in this scope of the paper focusing on vanadium-based type, the main reason of V-RFB / H_2SO_4 system chosen as an option for energy source is mainly based on its electrolyte stability (Kazacos et al., 1989; Li et al., 2007) and suitability and safely be used in many applications as long as the battery undergoes continuous cycling (Rahman et al., 1998). Furthermore, it's ruggedness edges against membrane crossover problem (Gattrell et al., 2004), hence prolong cell life cycle. Their fast response time and lower life cycle environmental effect (Noack et al., 2008) could also be attractive alternative to other type of energy storage.

4. Research opportunities for V-RFB

Much of the work reported in the past for V-RFB system has been focusing on the effort to improve poor kinetic reactions and energy density (Rahman et al., 1998; Gaku Oriji, 2004; Gattrell et al., 2004; Skyllas-Kazacos et al., 2004), conductivity of membrane (Mohammadi et al., 1995; Sukkar et al., 2004), potential redox couple (Skyllas-Kazacos, 2003; Tao et al., 2009), electrolyte stability (M. Skyllas-Kazacos et al., 1996; Rahman et al., 2009) and potential electrodes (Kazacos et al., 1989). Lately, since technology development of V-RFB reached piloted field demonstration and Shah *et al.* (Shah et al., 2008) started the two-dimensional model of V-RFB, it opens new research dimension with interest grows into modelling of V-RFB (Blanc et al., 2008; Al-Fetlawi et al., 2009; You et al., 2009). The following are further research opportunities for V-RFB.

4.1 V-RFB Characterisation

Skyllas-Kazacos et al. (Skyllas-Kazacos et al., 1991) highlighted general characteristics of V-RFB based on various applications. Specific characterizations of V-RFB performance on mobile application such as possibility to fully discharge without affecting the battery performance, possibility to discharge at different current level and no self-discharge during standby mode were also discussed in different literatures (Rychcik et al., 1988; Skyllas-Kazacos et al., 1991; Rahman et al., 2004; Skyllas-Kazacos, Retrieved on 24 Feb 2008, accessed on 07/07/2008). Nevertheless, the studies are concluded in general terms and no specific conclusion on overall performance of V-RFB implemented on their golf-cart, with respect to application in automotive industries. There is almost unknown in the literature regarding to the polarization effect of the battery as well as its electric circuit model. While various electric battery models have been proposed for different energy storage such as lead-acid, lithium-ion and nickel metal hydrate (Kiessling et al., 1995; Abu-Sharkh et al., 2004; Chen et al., 2006; Lynch et al., 2006), V-RFB would exhibits rather different characteristics to those systems. For example, in Li-ion battery, the system experiences hysteresis effect which would influence the system performance during charge – discharge cycle, whereas for V-RFB system, there is no suggestion in the literature for similar issue. While hysteresis effect would require longer relaxation time for dynamic response of the battery, it could be different with V-RFB.

4.2 Electric circuit modelling

Electrochemical models tend to be computationally time-consuming due to a system of coupled time-varying partial differential equations (Kroeze et al., 2008). Nevertheless, the information from the model could be used to understand the system better and reduce the time-consuming laboratory work. Previous work on the V-RFB system performed at University of Southampton, UK has suggested that there was no transient, two-dimension developed models for V-RFB of sufficient complexity to simulate experiment until it was proposed by Shah *et al.* (Shah et al., 2008). The model has been verified by experimental data and has shown the capability to demonstrate a good degree of accuracy in predicting the trends observed in a laboratory test, with respect to the variations in two key parameters of concentration and flow rate of V-RFB. The model was extended for two additional models using the same electrochemical model platform in view of hydrogen evolution on negative electrode (Shah et al., 2010) and thermal effects (Al-Fetlawi et al., 2009) which decrease the cell efficiency. Other electrochemical-based modelling effort on V-RFB also available presented by You *et al.* (You et al., 2009) and Blanc (Blanc et al., 2008; Blanc, 2009).

Even though these models has shown its capability to predict accurately the behaviour of the system and robust, which simplifies all hourly laboratory efforts, these models offer less application in circuit simulation software (Chen et al., 2006) such as PSpice applications, especially in assisting electrical engineer designers. Sharkh *et al.* (Abu-Sharkh et al., 2004) and Dees *et al.* (Dees et al., 2002) suggested that the electrochemical models best suited for optimization of the physical design aspects of electrodes and electrolytes. Moreover, this model requires details knowledge of kinetic reactions take place in the battery as well as its detail material properties, hence require extensive investigation.

Electric circuit equivalent models, on the other hand, are the most intuitive for use in the circuit simulation (Rao et al., 2003; Abu-Sharkh et al., 2004; Chen et al., 2006), which depicts the operational principle of the battery under pre-determined condition. Thevenin models are commonly used for equivalent circuit models, despite its limitation only for fixed state-of charge and temperature setting. Anyhow, an increase of RC networks in Thevenin model would increase its accuracy in predicting the battery response, especially its dynamic characteristics.

To date, only few works has been reported on electric circuit model for V-RFB. Chahwan *et al.* (Chahwan et al., 2007) has proposed simple equivalent circuit for V-RFB, which its model analysis has been tested in wind energy simulated systems by Barote *et al.*(Barote et al., 2009). Chahwan works are based on estimating of the losses experience by the system, even though there were no detail explanations on how the losses were estimated. Moreover, there was no comparison on their V-RFB model with other V-RFB characteristics data to prove that the losses assumption was made has proven to presenting a real behaviour of V-RFB system. Nonetheless, the works presented some parameters that require further attention for system losses such as parasitic, pump and other losses.

Therefore, there are opportunities in developing an equivalent circuit that would emulate the dynamic behaviour of the V-RFB system. To do this, accurate RC parameters need to be obtained to represent system characteristics. Different methods could be used in order to obtain the dynamic parameters of the battery such as linear parameter varying, spline technique, extended Kalman filter (EKF) etc.

Depending on applications, all parameter identification techniques would exhibit error depending on assumption made in the model. Linear parameter varying techniques exercise a battery within a linear region of state-of-charge, which represent a constant function of state-of-charge and temperature of the battery. While this method is rather simple and relatively effective, it does suffer from inherent transitional discontinuity; noise free measurement data required (Hu et al., 2008). Spline technique is relying on polynomial model of known data points, which the higher the polynomial degree, the better the model could emulate the actual system behaviour though it does not prevent overshooting problem at intermediate points. EKF anyhow, could estimate the states and parameters of dynamic behaviour of the system despite of the original data were contaminated with noisy measurements.

On the other hand, various suggestions of electric circuit model for proton exchange membrane fuel cell have been proposed (Yu et al., 2005; Lazarou et al., 2009). Since V-RFB has relatively similar in principle of operation, there are possibilities to the employ a similar approach in constructing the electric circuit model.

4.3 RFB for HEVs Applications

V-RFB offers potential advantages over other types of RFBs such as lack of cross-contamination due to diffusion of ions across the membrane, deep charge/discharge cycles, longer service life, and maintenance-free (Rychcik et al., 1988; Miyake et al., 2001).

V-RFB has been used in many applications (Miyake et al., 2001) and significant research on V-RFBs is on-going in our laboratory to optimize the chemistry and mechanical design, develop mathematical models, and research into battery management systems (Radford et al.; Ponce-de-León et al., 2006; Ponce-de-Leon et al., 2007; Pletcher et al., 2008; Shah et al., 2008). Few studies have been involved the use of RFBs for automotive applications. To date, there is only one study being reported had implemented RFB for powering vehicles, i.e. electric golf cart in The University of New South Wales (UNSW), Australia (Menictas et al., 1994; Skyllas-Kazacos, Retrieved on 24 Feb 2008, accessed on 07/07/2008). This is probably due to the claim that RFBs have low specific energy of 25–35 W h kg^{-1}, which has limited their use in electric vehicle or other mobile applications (Skyllas-Kazacos, 2003); noted that the maximum vanadium ion concentration that can be employed over wide range of temperature is typically 2 mol dm^{-3} and 3 mol dm^{-3} for narrower temperature range of 15 – 40 ^{o}C. Moreover, the solubility of V^{2+} and V^{3+} ion in sulfuric acid supporting electrolyte at temperature below 5 ^{o}C is delimited and stability of V^{5+} at temperature above 40 ^{o}C is predicted (M. Kazacos et al., 1990; M. Skyllas-Kazacos et al., 1996; Rahman et al., 1998).

Nevertheless, in contrast to previous report from the same group, two-person electric car assembled from commercially available elements and fitted with a 5 kW h vanadium battery could cover a distance of approximately 150 km with a speed of up to 70 km h^{-1} (Rychcik et al., 1988) with suggestion of at least 3 mol dm^{-3} vanadium concentration is required for EV applications (Rahman et al., 1998). Therefore, on our accord, we would consider that there's no conclusive argument that no possibility of V-RFB to be used as one of energy storage for mobile application.

The energy density of the vanadium battery is in the same range as those of the advanced lead-acid or nickel-cadmium batteries (Rychcik et al., 1988). The results from studies performed at the University of Southampton show that the V-FRB is comparable to the lead-acid battery and has an opportunity to be implemented for transportation (Mohamed et al., 2009). Recent laboratory tests at UNSW have indicated that there is room for further improvement in the parameters of the vanadium redox system. This has been supported by F. Rahman *et al.* (Rahman et al., 2004), which further work is currently underway at UNSW for 80 W h kg^{-1} by in-situ regeneration of V(V) using air oxidation of the discharged V(IV) solution allowing twice the driving range to be achieved in electric vehicle applications than previously reported by same group in UNSW. This study considered electric vehicles which obviously will require larger battery storage, hence decelerate the opportunity of the implementation of RFB for automotive applications. Anyhow, the finding proves that RFB is significant for automotive execution.

On the other hand, initial search for literature addressing HEV is more viable option for current automotive implementation (Williamson et al., 2005; Mohamed et al., 2009) and would provide a significant compromise in the overall system. To date, there are no reported studies suggested RFBs had been implemented in HEV system. As the name implies, HEV merges a conventional ICE-propulsion system with a rechargeable energy storage system (RESS). Regardless of any HEV configuration is used, HEV requires smaller energy storage than what BEV should have. This would fit with current technology status of RFB.

4.4 Energy management of RFB for HEVs application

HEV compromise a poor driving mileage in BEV and fumed-emissions in ICEs. Thus, it is important to optimize not only the architecture and components of the HEVs, but also the energy management strategy of the vehicle (Salman et al., 2005). Previous studies performed at UNSW proved that V-RFB is possible to provide traction power for EV with bulky design of V-RFB is expected for commercialization, but smaller design of V-RFB is possible with proper arrangement with ICE in HEV system. Obviously, to compromise both ICE and V-RFB it would requires a good energy management strategy to achieved best performances of both systems. Even though various energy management strategies have been proposed for different types of energy storage but the advantage of V-RFB as proposed by Skyllas-Kazacos *et al.* (Skyllas-Kazacos et al., 1986) over other types of energy storage would definitely requires a different energy management strategies to optimise both ICE and V-RFB.

No discussion found in the literature regarding to regenerative braking effect towards RFB as battery's capacity recovery is suggested through a rapid recharging of electrolytes (replacing the electrolytes) but not through direct capturing reverse kinetic energy during braking. Therefore, no conclusion is known over the effect of cycle life or storage capacity of V-RFB if V-RFB captures this reverse kinetic energy during its discharging period; does V-RFB has same memory effect as observed in nickel cadmium rechargeable batteries. No conclusion mentioned in the literature over the requirement of nitrogen–oxygen free environment during discharging period. Moreover, it is also important to know the effect of V-RFB performance over a fluctuation ups and down of the discharge rate of the battery from a vicious load in automotive application.

Obviously, energy management strategy for V-RFB or any other type of RFB in HEV should consider various factors such as degree of hybridization, fuel economy versus emissions target of the HEV, state-of-health of the battery etc. An offline-based optimization (such as genetic algorithm) process for RFB management strategies in HEV environment could be implemented to achieve optimum setting based on desired target. For example, if the system is to achieve best performance with good state-of-health of the battery, the optimization process should provide optimum solution in according to the proposed energy management strategies. The optimization process, which can only be carried out in the offline mode, is a complicated and a time-consuming task, and hence requires high computational capabilities. Obviously, the optimized settings will be valid only for certain operating conditions and have to be recomputed after each variation / setting. Hence, it is important to standardize a simple management method. On the other hand, there are also possibilities to employ some other energy storage into the traction system such as ultracapacitor to support RFB in propelling vehicle, as reported in many research of FCEV (Van Mierlo et al., 2004; Burke, 2007), with relatively more complex energy management strategies is expected.

5. Conclusion

Despite the advantages offered by the RFB, the technology is still emerging and has a long way to go before it can meet the demands in both large scale and automotive industries. Some of the materials used in RFBs, e.g. vanadium electrolytes require careful sourcing. The low energy density of RFB compared to the more established technology of conventional lead-acid or lithium-ions batteries still requires further attention.

Judging from the literature, to date, most of the studies on V-RFB system have been focusing on electrolyte species with different combination redox species, different molarities of vanadium and vanadium prepared in different supporting electrolyte in attempt to improve the low energy density of V-RFB. There is almost unknown in the literature regarding to the polarization effect of the battery as well as its electric circuit model. While various electric battery models have been proposed for different energy storage such as lead-acid, lithium-ion and nickel metal hydrate, theoretically V-RFB would exhibits rather different characteristics to those systems. Lack of reliable data to support modelling characterization of V-RFB in the literature is another important issue need to be catered. There are still issues on V-RFB’s engineering aspect such as effect of different material properties, different pressure on cell stack, contact of electrodes as well as reduction of impedance that require exploration.

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References

Abu-Sharkh S and Doerffel D (2004). "Rapid test and non-linear model characterisation of solid-state lithium-ion batteries." Journal of Power Sources **130**(1-2): 266-274.

Al-Fetlawi H, Shah AA and Walsh FC (2009). "Non-isothermal modelling of the all-vanadium redox flow battery." Electrochimica Acta **55**(1): 78-89.

Barote L, Marinescu C and Georgescu M (2009). VRB modeling for storage in stand-alone wind energy systems. PowerTech, 2009 IEEE Bucharest.1-6

Blanc C (2009). "Modeling of a vanadium redox flow battery electricity storage system." Laboratoire d'Electronique Industrielle **PhD Thesis**: 263.Available

Blanc C and Rufer A (2008). Multiphysics and energetic modeling of a vanadium redox flow battery. IEEE International Conference on Sustainable Energy Technologies, ICSET2008, Singapore, IEEE.696-701

Burke AF (2007). Batteries and ultracapacitors for electric, hybrid, and fuel cell vehicles. Proceedings of the IEEE.806-820

Chahwan J, Abbey C and Joos G (2007). VRB Modelling for the Study of Output Terminal Voltages, Internal Losses and Performance. IEEE Canada Electrical Power Conference, 2007. EPC 2007.387-392

Chen H, Cong TN, Yang W, Tan C, Li Y and Ding Y (2009). "Progress in electrical energy storage system: A critical review." Progress in Natural Science **19**(3): 291-312.

Chen M and Rincon-Mora GA (2006). "Accurate electrical battery model capable of predicting runtime and I-V performance." IEEE Transactions on Energy Conversion **21**(2): 504-511.

Cook B (2002). "Introduction to fuel cells and hydrogen technology." Engineering Science And Education Journal: 205-216.

Dees DW, Battaglia VS and Bélanger A (2002). "Electrochemical modeling of lithium polymer

batteries." Journal of Power Sources **110**(2): 310-320.
Dhameja S (2002). Electric vehicle battery systems. Woburn, Newnes Press.
Fedkiw PS and Watts RW (1984). "A mathematical model for the iron/chromium redox battery." Journal of The Electrochemical Society **131**(4): 701-709.
Gaku Oriji YK, Takashi Miura (2004). "Investigation on V(IV)/V(V) species in a vanadium redox flow battery." Electrochimica Acta **49**(19): 3091-3095.
Gattrell M, Park J, MacDougall B, Apte J, McCarthy S and Wu CW (2004). "Study of the Mechanism of the Vanadium 4+/5+ Redox Reaction in Acidic Solutions." Journal of The Electrochemical Society **151**(1): A123-A130.
Gonzalez A, Gallachóir BÓ, McKeogh E and Lynch K (2004) "Study of electricity storage technologies and their potential to address wind energy intermittency in Ireland."Available<http://www.sei.ie/uploadedfiles/FundedProgrammes/REHC03001FinalReport.pdf> accessed 03015 June 02009.
He X, Maxwell T and Parten M (2006). "Development of a hybrid electric vehicle with a hydrogen-fueled IC engine." IEEE Transactions on Vehicular Technology **55**(6): 1693-1703.
Hebner R, Beno J and Walls A (2002). "Flywheel batteries come around again." Spectrum, IEEE **39**(4): 46-51.
Hu Y, Yurkovich S, Guezennec Y and Bornatico R (2008). Model-based calibration for battery characterization in HEV applications. American Control Conference, 2008.318-325
Husain I (2003). Electric and hybrid vehicles: Design fundamentals. Boca Raton, Florida, CRC Press.
J. A. Smith, M. H. Nehrir, V. Gerez and Shaw aSR (2002). "A broad look at the workings, types, and applications of fuel cells." Power Engineering Society Summer Meeting 2002, IEEE **1**: 70-75.
J. Larminie and Lowry J (2003). Electric vehicle technology explained. West Sussex, John Wiley & Sons, ltd.
Joerissen L, Garche J, Fabjan C and Tomazic G (2004). Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems, Ulm, Germany, Elsevier.98-104
Kazacos M and Skyllas-Kazacos M (1989). "Performance Characteristics of Carbon Plastic Electrodes in the All-Vanadium Redox Cell." Journal of The Electrochemical Society **136**(9): 2759-2760.
Kiessling R and Mills J (1995). A battery model for the monitoring of, and corrective action on, lead/acid electric-vehicle batteries, Journal of Power Sources.339-340
Kondoh J, I. Ishii, H. Yamaguchi, A. Murata, K. Otani, K. Sakuta, N. Higuchi, Sekine S and Kamimoto M (2000). "Electrical energy storage systems for energy networks." Energy Conversion and Management **41**(17): 1863-1874.
Koshizuka N, Ishikawa F, Nasu H, Murakami M, Matsunaga K, Saito S, Saito O, Nakamura Y, Yamamoto H, Takahata R, Itoh Y, Ikezawa H and Tomita M (2003). "Progress of superconducting bearing technologies for flywheel energy storage systems." Physica C: Superconductivity **386**: 444-450.
Kroeze RC and Krein PT (2008). Electrical battery model for use in dynamic electric vehicle simulations. IEEE Power Electronics Specialists Conference, 2008. PESC 2008. .1336-1342
Lazarou S, Pyrgioti E and Alexandridis AT (2009). "A simple electric circuit model for proton exchange membrane fuel cells." Journal of Power Sources **190**(2): 380-386.
Li X, Zhang H, Mai Z, Zhang H and Vankelecom I (2011). "Ion exchange membranes for vanadium redox flow battery (VRB) applications." Energy & Environmental Science **4**(4): 1147-1160.
Li XG, Huang KL, Liu SQ, Tan N and Chen LQ (2007). "Characteristics of graphite felt electrode electrochemically oxidized for vanadium redox battery application." Transactions of Nonferrous Metals Society of China **17**(1): 195-199.
Lynch WA and Salameh ZM (2006). Electrical component model for a nickel-cadmium electric vehicle traction battery, Piscataway, NJ, USA, 2006 IEEE Power Engineering Society General Meeting.5 pp.
M. Kazacos, M. Cheng and Skyllas-Kazacos M (1990). "Vanadium redox cell electrolyte optimization studies." Journal of Applied Electrochemistry **20**: 463-467.
M. Skyllas-Kazacos, C. Menictas and Kazacos M (1996). "Thermal stability of concentrated V(V) electrolytes in the vanadium redox cell." Journal of the Electrochemical Society **143**(No. 4): L86–L88.
Menictas C, Hong DR, Yan ZH, Wilson YJ, Kazacos M and Skyllas-Kazacos M (1994). Status of the vanadium redox battery development program. National Conference Publication - Institution of Engineers, Australia, Sydney, USA, IE Aust, Crows Nest, NSW, Aust.299-303
Miyake S and Tokuda N (2001). Vanadium redox-flow battery for a variety of applications. IEEE Power Engineering Society Summer Meeting, 2001. .450-451 vol.451
Mohamed MR, Sharkh SM and Walsh FC (2009). Redox flow batteries for hybrid electric vehicles: progress and challenges. The 5th International IEEE Vehicle Power and Propulsion Conference (VPPC'09), Dearborn, Michigan, IEEE.551-557
Mohammadi T and Skyllas-Kazacos M (1995). "Characterisation of novel composite membrane for redox flow battery applications." Journal of Membrane Science **98**(1-2): 77-87.
N. Tokuda, T. Kanno, T. Hara, T. Shigematsu, Y Tsutsui, A. Ikeuchi, T Itou and Kumamoto. T (2000). "Development of redox flow battery system." SEI Technical Review June 2000 **No. 50**: 88-94.
Noack JN, Vorhauser L, Pinkwart K and Tuebke J (2008). "Vanadium Redox Flow Batteries : An In-Depth Analysis." Society **3**(**3**): 2010-2010.Available<http://mydocs.epri.com/docs/public/000000000001014836.pdf> accessed on 20 October 2010.
Pathak S, Das JN, Rangarajan J, Choudhury SR and Prakash R (2006). Development of prototype phosphoric acid fuel cell pick-up electric vehicle. IEEE Conference ICEHV '06. .1-4
Pera MC, Hissel D and Kauffmann JM (2002). Fuel cell systems for electrical vehicles. IEEE 55th Vehicular Technology Conference, 2002. VTC Spring 2002. .2097-2102 vol.2094
Pletcher D, Hantao Z, Kear G, Low CTJ, Walsh FC and

Wills RGA (2008). "A novel flow battery - a lead-acid battery based on an electrolyte with soluble lead (II). Part VI. studies of the lead dioxide positive electrode." Journal of Power Sources **180**(1): 630-634.
Ponce-de-León C, Frías-Ferrer A, González-García J, A.Szánto D and Walsh FC (2006). "Redox flow cells for energy conversion." Journal of Power Sources **160**(1): 716-732.
Ponce-de-Leon C, Reade GW, Whyte I, Male SE and Walsh FC (2007). "Characterization of the reaction environment in a filter-press redox flow reactor." Electrochimica Acta **52**(19): 5815-5823.
Radford GJW, Cox J, Wills RGA and Walsh FC "Electrochemical characterisation of activated carbon particles used in redox flow battery electrodes." Journal of Power Sources **In Press, Accepted Manuscript**.
Rahman F, Habiballah IO and Skyllas-Kazacos M (2004). "Electrochemical behavior of vanadium electrolyte for vanadium redox battery - a new technology for large scale energy storage systems." Cigre 2004 Session Proceedings **-**(Session): 1-8.
Rahman F and Skyllas-Kazacos M (1998). "Solubility of vanadyl sulfate in concentrated sulfuric acid solutions." Journal of Power Sources **72**(2): 105-110.
Rahman F and Skyllas-Kazacos M (2009). "Vanadium redox battery: Positive half-cell electrolyte studies." Journal of Power Sources **189**(2): 1212-1219.
Rao R, Vrudhula S and Rakhmatov DN (2003). "Battery modeling for energy aware system design." Computer **36**(12): 77-87.
Romm JJ (2004). The hype about hydrogen: Fact and fiction in the race to save the climate. Washington DC, Island Press.
Rychcik M and Skyllas-Kazacos M (1988). "Characteristics of a new all-vanadium redox flow battery." Journal of Power Sources **22**(1): 59-67.
S. G. Chalk and Miller JF (2006). "Key challenges and recent progress in batteries, fuel cells, and hydrogen storage for clean energy systems." Journal of Power Sources **159**(1): 73-80.
Salman M, Chang MF and Chen JY (2005). Predictive energy management strategies for hybrid vehicles. IEEE Vehicle Power and Propulsion Conference, VPPC 2005. VPPC'05.
Shah AA, Al-Fetlawi H and Walsh FC (2010). "Dynamic modelling of hydrogen evolution effects in the all-vanadium redox flow battery." Electrochimica Acta **55**(3): 1125-1139.
Shah AA, Watt-Smith MJ and Walsh FC (2008). "A dynamic performance model for redox-flow batteries involving soluble species." Electrochimica Acta **53**(27): 8087-8100.
Skyllas-Kazacos M (2003). "Novel vanadium chloride/polyhalide redox flow battery." Journal of Power Sources **124**: 299-302.
Skyllas-Kazacos M (Retrieved on 24 Feb 2008, accessed on 07/07/2008). "Recent progress with the USNW vanadium battery." Available <http://www.arizonaenergy.org/Analysis/FuelCell/Vanadium%20Battery/recent_progress_with_the_unsw_va.htm> accessed on 07/07/2008.
Skyllas-Kazacos M, Chakrabarti MH, Hajimolana SA, Mjalli FS and Saleem M (2011). "Progress in Flow Battery Research and Development." Journal of The Electrochemical Society **158**(8): R55-R79.
Skyllas-Kazacos M, Kasherman D, Hong DR and Kazacos M (1991). "Characteristics and performance of 1 kW UNSW vanadium redox battery." Journal of Power Sources **35**(4): 399-404.
Skyllas-Kazacos M and Limantari Y (2004). "Kinetics of the Chemical Dissolution of Vanadium Pentoxide in Acidic Bromide Solutions." Journal of Applied Electrochemistry **34**(7): 681-685.
Skyllas-Kazacos M and Menictas C (1997). The vanadium redox battery for emergency back-up applications. 19th International Telecommunications Energy Conference, 1997. INTELEC 97., .463-471
Skyllas-Kazacos M and Robins RG (1986). "All vanadium redox battery." **4786567**(4786567).Available
Sukkar T and Skyllas-Kazacos M (2004). "Membrane stability studies for vanadium redox cell applications." Journal of Applied Electrochemistry **34**(2): 137-145.
Tao H and Fangqin X (2009). Investigation on Manganese (Mn2+/Mn3+) - Vanadium (V2+/V3+) Redox Flow Battery. Power and Energy Engineering Conference, 2009. APPEEC 2009. Asia-Pacific.1-4
Van Mierlo J, Van den Bossche P and Maggetto G (2004). "Models of energy sources for EV and HEV: fuel cells, batteries, ultracapacitors, flywheels and engine-generators." Journal of Power Sources **128**(1): 76-89.
Williamson SS and Emadi A (2005). "Comparative assessment of hybrid electric and fuel cell vehicles based on comprehensive well-to-wheels efficiency analysis." IEEE Transactions on Vehicular Technology **54**(3): 856-862.
You D, Zhang H and Chen J (2009). "A simple model for the vanadium redox battery." Electrochimica Acta **54**(27): 6827-6836.
Yu D and Yuvarajan S (2005). "Electronic circuit model for proton exchange membrane fuel cells." Journal of Power Sources **142**(1-2): 238-242.

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