

Assessing Damage to Graphite Electrodes in Bromine Redox Flow Battery Systems

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ABSTRACT

The transition from our gross dependence on fossil fuels to sustainably harvesting renewable power presents both economic and technological challenges. A major drawback with renewable resources is that the power output is dependent on environmental factors outside of our ability to control. This allows either power output to exceed or fall short of forecast levels which may lead to grid instabilities. Therefore, large scale energy storage systems are critical to store excess power when the output exceeds demand and to supplement output power when it falls short of demand. A promising technology to meet this growing need is the zinc bromide redox flow battery. Unfortunately the cause for performance degradation within this system is still poorly understood. Reported is an analytical method for assessing damage from both oxidative and reductive aging of graphite electrodes in concentrated bromine electrolytes.

Keywords: renewable power, large scale energy storage, cycle life, performance degradation, graphite electrodes

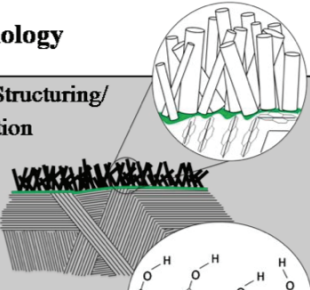
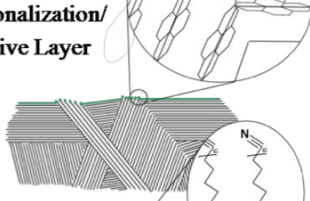
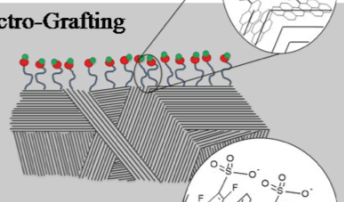
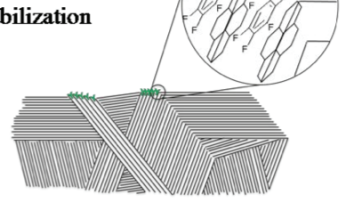
1 INTRODUCTION

The zinc bromide Redox Flow Battery (RFB) is a commercially available energy storage technology, which has extremely attractive attributes for Large Scale Energy Storage (LSES) applications [1-4]. The redox couples are $\text{Br}^-/\text{Br}_2^0$ at the positive electrode and $\text{Zn}^{2+}/\text{Zn}^0$ at the negative electrode. In recent years this technology was selected for several private and government funded grid scale energy storage projects because it is an easily scalable device, with

design/operation flexibility, fast response time, deep-discharge capability, and long expected cycle life [5-7]. It is evident that RFBs have not matured much since their initial development in the late 70's [8] – this is widely agreed to be attributed to the perceived low cost effectiveness of the technology which is in part due to performance degradation. Understanding the primary degradation mechanism(s) and rate thereof is essential to addressing cycle life issues and enable practical large-scale applications of an otherwise front-runner technology. The chemistry for the zinc bromide RFB at the positive electrode has been previously studied and operation models proposed [9-12]. Despite these efforts and a better overall understanding of the system chemistry the limitations on cycle life capacity, and specifically the electrode performance degradation mechanisms, is yet to be adequately explained.

There has been a tremendous effort towards better understanding graphite surface chemistry; a great deal more is anticipated with the emergence of graphene and its potential to be used as electrode material [13-16]. The degradation of graphitic materials is generally explained by the formation of intermediate functional groups, which are expected to affect the mechanical stability and electrocatalytic activity of the exposed surface. A time dependent change in the charge density at the electrode-solution interface can be explained by adsorption of electroinactive contaminants or in general by chemical changes on the electrode surface [17, 18]. The specific functional group intermediates that form at the electrode-solution interface were not quantified as part of this work; it suffices to say that there exists evidence of certain functional groups that have been shown to catalyze undesired and irreversible reactions at carbon surfaces [19-23].

Table 1 State of the art in modified electrode materials.

Technology	Contributing Author(s)	Key Benefit(s)	Key Issue(s)
 <p>Nano-Structuring/ Activation</p>	Banks et al 2004, Li et al 2006, Tseng et al 2006, Yang et al 2007, Guo et al 2008, Liu et al 2012, Manahan et al 2013, Lai et al 2013 [26-34]	Increased surface area and apparent electro-catalytic activity	Susceptible to loss of electro-catalytic activity, difficult to scale-up, cannot be implemented after stack is assembled
 <p>Functionalization/ Protective Layer</p>	Murray 1980, Anson et al 1980, Kamau et al 1985, Zhao et al 2005, Wang and Wang 2007, Shen et al 2008, Shao et al 2009, Yue et al 2010, Fan et al 2011, Madec et al 2011, Abd-El-Aziz 2012, Flox et al 2013, Yao et al 2012, Liu et al 2012, Xu et al 2012, Di Blasi et al 2013, Gao et al 2013 [22, 35-50]	Increased electro-catalytic activity, anti-oxidative performance	Susceptible to loss of electro-catalytic activity, short lived in extreme oxidative environments, impractical with commercial devices
 <p>Electro-Grafting</p>	Guadalupe and Abruna 1985, Chai et al 2000, Vase et al 2005, Jin et al 2005, Bashyam and Zelenay 2006, Verma et al 2010, Weissmann et al 2010, Belanger and Pinson 2011, Kang and Lee 2013, Oliveira et al 2013 [51-60]	Reaction selectivity, specific ion sensitivity (sensors)	Susceptible to loss of electro-catalytic activity, cannot be implemented after stack is assembled, impractical with commercial devices
 <p>Stabilization</p>	Bistrika et al 2013 [61]	Long term preservation of electro-catalytic activity	Use of Hydrofluoric acid in treatment process

Although not directly pertaining to zinc bromide RFBs, Liu et. al. investigated the corrosion of the positive electrode in all vanadium RFBs, and it ought to be mentioned since it was found that the erosion mechanism could be attributed to the evolution of carbon dioxide in highly oxidative environments [24]. This arguably arises from the undesired water electrolysis reaction present in all aqueous systems. Other factors that might lead to degradation have been the topic(s) of speculative argument; e.g., changes in electrocatalytic properties [25] and extent of electronic coupling at the electrode-solution interface [21] can be argued to arise out of asymmetric surface resistivity. Liu et al. suggest that it is possible to induce localized potential gradients that could result in accelerated rates of corrosion at affected sites. However, unless the electrode assembly is very unique it is unlikely that asymmetry in surface resistivity would give rise to localized overpotential gradients, but more likely that localized current density gradients might be established. The localized current density gradients could give rise to accelerated gas evolution rates in aqueous systems as well as a more rapid elimination of the electrochemically active sites.

Modifying electrode surfaces for added benefit is not a novel concept. Particularly within the arguably dormant

hydrogen fuel cell industry where researchers, as well as large global corporations with a vested interest, have long searched for the holy grail in modified electrodes, i.e., the alternative to precious metal catalysis. Table 1 provides a more extensive review of some of the major work in the field of modified carbon electrodes [26-34],[22, 35-50],[51-60],[61].

2 EXPERIMENTAL

Bromide salts and reagents were purchased from Sigma Aldrich chemical company and used as received. Graphite electrodes were purchased from Graphtek LLC and modified by polishing the working surface with 2000 (ultra fine) grit sand paper and cleaned in a sonic bath.

2.1 Chemical Synthesis

N-Methyl-n-Ethyl Pyrrolidinium Bromide ($C_7H_{16}BrN$), is the complexing agent used in the battery electrolyte. It was synthesized from n-Methyl Morpholine ($C_5H_{11}NO$) and Bromoethane (C_2H_5Br). This was done by adding 1:1 C_2H_5Br to $C_5H_{11}NO$ in Tetrahydrofuran (THF, C_4H_8O). The C_2H_5Br was added drop wise ($\sim 25 \text{ ml hr}^{-1}$) to a mixture (1:1 well mixed) of $C_5H_{11}NO$ in THF at 120-140 °C. The mixture was

refluxed for 8 hours to ensure reaction completion. The mixture was allowed to cool and product was precipitated by addition of sufficient hexanes (C₆H₁₄). Product was purified by recrystallization from hot THF/Hexanes with a 96% yield. The finished product was stored under nitrogen in a moisture free environment.

2.4 Experimental Set Up

As part of this work both a 2-electrode cycling cell and 3-electrode analytical test cell was used; depicted in Figure 1.

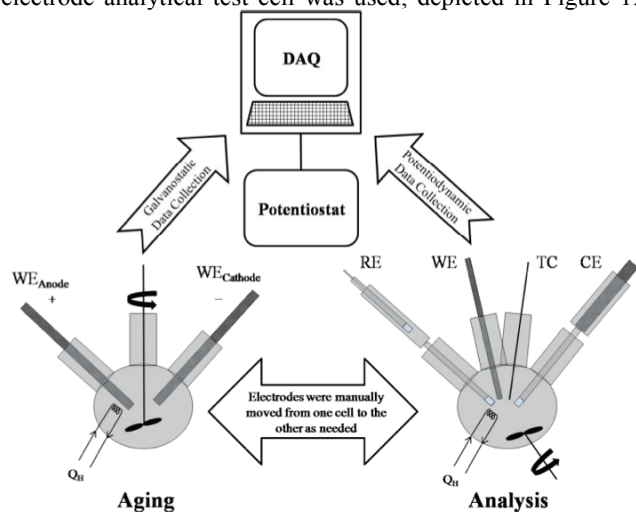
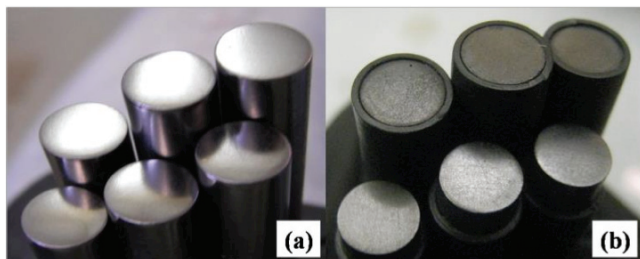


Figure 1 Experimental flow diagram and test cell layout.

The performance of the in-lab manufactured Ag/AgBr reference probes was checked against the [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ redox couple and found to be in good agreement with that reported in literature.



3 RESULTS AND CONCLUSIONS

Performance degradation is a result of both physical and chemical erosion. The physical erosion could be readily observed by visual inspection (see Figure 2 below), while the

Figure 2 (a) newly prepared and (b) aged electrodes.

chemical erosion, and permanent activity loss was qualitatively reached by analytically measuring the Tafel parameters, i_0 and α , which are the exchange current density and transfer coefficient, respectively. The steady state current density, i_{ss} , can be accurately predicted by the Butler-Volmer model at relatively low overpotentials.

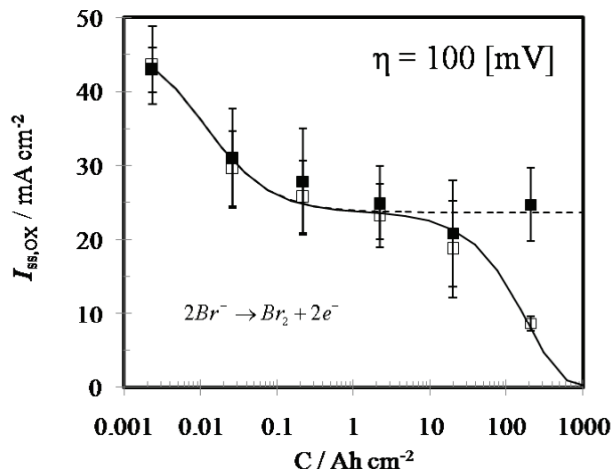


Figure 3 Steady state oxidation current for an applied 100 [mV] over-potential after cathodic (•) and anodic (◻) aging.

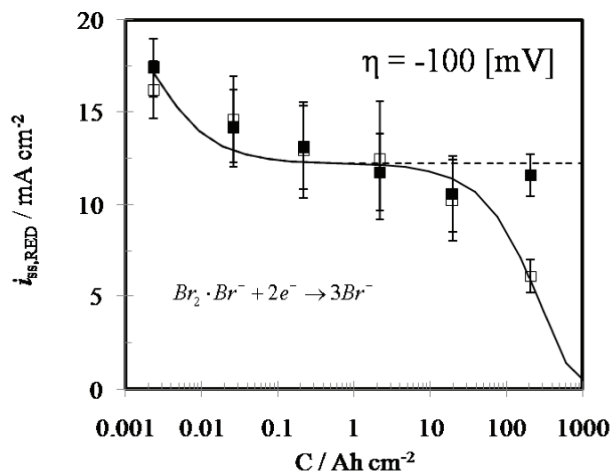


Figure 4 Steady state reduction current for an applied 100 [mV] over-potential after cathodic (•) and anodic (◻) aging.

The result is plotted as a function of the charge passed through the electrode and depicted in Figures 3 and 4, representing the forward and reverse bromide reaction as the electrodes are aged cathodically and anodically, respectively. Oxidative damage can be isolated as the primary of eventual electrode death, while the performance degradation arising from continuous reduction does not appear to be as serious for either reaction.

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