Direct visualization of reactant transport in forced convection electrochemical cells and its application to redox flow batteries

Javier Rubio-Garcia, Anthony Kucernak⁎, Alexandra Charleson

Department of Chemistry, Imperial College London, SW7 2AZ, UK

A R T I C L E   I N F O

Keywords: Energy storage Redox flow battery Mass transport Visualization Electrochemiluminescence

A B S T R A C T

A novel, simple and low cost electrochemiluminescence imaging method for monitoring mass transport phenomena in a redox flow battery-like system is presented. Luminol solutions were pumped through a flow field (FF) with a given design. At the flowfield/electrode interface light is emitted upon dye oxidation allowing direct visualization of channels, U-bends and regions of poor wetting. Image analysis allows direct visualization of reactant distribution and poor mass transport through tortuous materials. These results were compared with the experimental performance of an all-vanadium redox flow battery with different FFs as a function of flow and good correlation achieved.

1. Introduction

Redox Flow Batteries (RFB) are one of the most promising systems for medium to large scale energy storage due to its versatility and fast response [1]. Despite recent efforts in improving cell design [2–4], electrode kinetics [5–7] and energy density [8]; the widespread implementation of RFBs is hindered by high capital cost. Higher electrolyte utilisation – in terms of improved state of ultimate charge (SoC) and increased local reaction rates (leading to lower stoichiometries at constant flow) - would be advantageous to improve energy density and round trip efficiency. This could be achieved with a better understanding of mass transport processes within the RFB which have traditionally been studied using mathematical models with different flow field (FF) designs [9, 10]. In-operando visualization techniques have been reported in the literature for polymer electrolyte membrane fuel cells (PEFCs) to investigate processes such as flow velocity [11], temperature mapping [12] or water distribution during fuel cell operation. [13, 14] These offer valuable insights into processes which are difficult to predict with mathematical models such as the wetting of tortuous electrodes or degradation of components. Few studies on the direct visualization of reactant transport in RFBs are available in the literature. Houser et al. employed visualization of electrolyte distribution using a thermally responsive layer [15]. Wong et al. investigated reactant transport by means of fluorescence microscopy revealing the importance of the electrode microstructure to achieve homogeneous reactant distribution [16]. Previously, we utilised chemiluminescence approaches to understand oxygen concentration distribution within PEFC catalyst layers [17, 18]. Here, we present a method based on electrochemiluminescent (ECL) reactions which allow us to visualize mass transport phenomena in liquid electrolytes and correlate that with processes occurring within the RFB.

2. Experimental

The experimental configuration is shown in Fig. 1A. The reactor consists of FF designs machined from electrically insulating glass reinforced epoxy (GRP) board interposed between the working and counter electrodes. A Grafoil counter electrode was laminated to one face of the FF using pre-pregs (Arlon 47 N). A 50x50mm ITO glass window was attached to the other face of the FF and held in place with a Copper coated GRP board. The window was electrically connected to the Copper layer using an electrically conductive gasket. Fig. 1B-D depicts the light emitting reaction occurring during experiments. Reaction occurs only at the ITO layer when studying either no, or electrochemically inactive materials (glass fibre paper) are studied. When the ITO is in contact with the porous electrically conductive carbon electrode, Fig. 3D, both materials become part of an “extended” working electrode.

Luminol (Sigma-Aldrich, ≥ 97%) solutions (4.5–72 mM) were prepared in 0.1 M sodium hydroxide (NaOH, VWR, 99%) with 1 vol% hydrogen peroxide (VWR,30%) using ultrapure “MilliQ” water (18.2MΩ). Porous media were glass fibre filter paper (Whatman®, 1825-150) or carbon paper (SGL-GDL-10-AA, SGL, Germany). A constant flow of Luminol solution was pumped through the pseudo RFB cell with a peristaltic pump (Watson-Marlow, 120 U). A silicon photodiode (ThorLabs,SM05PD1A) was positioned 19 mm and at an angle of 49° to the copper layer using an electrically conductive gasket. Fig. 1B-D depicts the light emitting reaction occurring during experiments. Reaction occurs only at the ITO layer when studying either no, or electrochemically inactive materials (glass fibre paper) are studied. When the ITO is in contact with the porous electrically conductive carbon electrode, Fig. 3D, both materials become part of an “extended” working electrode.

⁎ Corresponding author.

E-mail address: anthony@imperial.ac.uk (A. Kucernak).

https://doi.org/10.1016/j.elecom.2018.07.002
Received 31 May 2018; Received in revised form 2 July 2018; Accepted 2 July 2018
Available online 03 July 2018
3. Results and discussion

An electrochemical reactor with either a serpentine or interdigitated FF was constructed. This allowed us to utilise the light emitted from the radiative decomposition of oxidized dye intermediates to investigate reactant distribution for different compositions and flow rate. The counter reaction (hydrogen evolution) occurs in the same electrolyte and no membrane or separator was used. We selected luminol as the probe molecule owing to its water solubility and tunability of emission lifetime via increasing pH [19]. This was important as it ensured that the radiative processes occur in close vicinity to the surface of the electrode and increases the spatial resolution of our approach. The Luminol reaction is an EC process where the electrochemically oxidized Luminol molecule reacts homogeneously with hydrogen peroxide to produce light and N₂, Fig. 1(A) [19].

Validation of our reactor was conducted by running 60s potentiostatic experiments and detecting the light emitted both with the camera and photodiode. Pixel integration of images were correlated with the photodiode reading as a function of dye concentration (Fig. 2A). At low dye concentrations there was a deviation due to poor camera operation under low light conditions. As a result, we relied on the photodiode response to investigate concentration effects. Regardless of the FF design, serpentine (square) and interdigitated (circle), a linear relationship between dye concentration and light emission is found below 25 mM followed by deviation at higher concentrations. Under similar conditions this diversion from linearity has been attributed to self-quenching reactions [20].

Engstrom et al. showed how dye electrolyte formulation is crucial to investigate electrode reactive sites at a carbon electrode with reliable results [21]. Hence, we decided to investigate the effect of flow rate with a dye concentration within the linear region (8.25 mM). Fig. 1B shows the average photodiode reading for flow rate ranges between 10 and 135 mL min⁻¹, which are typical values used within RFBs of this size. The inset shows the stability of the response over time. After an initial light spike most likely associated with luminol adsorption on the ITO, constant values were obtained. A gradual increase in photocurrent, from 1.8 nA at 10 mL min⁻¹ to 4.2 nA at 135 mL min⁻¹ is observed for the serpentine FF which suggests greater reaction at higher flow rates. This effect is even more pronounced for the interdigitated pattern as this design is known to enable larger transport towards the electrode, greater turbulence, and hence larger pressure drop [15]. If we assume the flow is majorly through the channel and using the hydraulic diameter of the channel we calculate the Reynolds number for our ECL reactor of < 250 for serpentine and interdigitated FFs at 135 mL min⁻¹ – values in the laminar regime. Stagnant zones may occur at corners for both FFs and at the end of dead-ended channels for the interdigitated FFs. For both designs the photocurrent increase is sub-linear. This could be associated with changes in the thickness of the boundary layer within the electrode structure or mass transport limitations. Such effects are well established in other electrochemical systems e.g. in PEFCs using laser Doppler anemometry [11], and chemiluminescence in fuel cell FFs [17, 18]. However, light emission self-quenching reactions due to high local luminol concentration cannot be ruled out. The latter hypothesis is supported by the determination of ECL emission lifetime using pulsed chronoanopscopy and evaluating light emission decay in subsequent camera images. An increase in flow rate from 20 mL min⁻¹ to 60 mL min⁻¹ led to a decrease of emission lifetime from 0.5 s to 0.25 s. This effect is associated with side reactions which capture the intermediated before light can be emitted [22] and is more pronounced for the interdigitated FF design.

The behaviour of the ECL reaction within the RFB-like electrochemical reactor was compared with performance of an all-vanadium Scm⁻² RFB in which V(II) oxidation and V(V) reduction take place at the cell and amplified (ThorLabs, PDA200C) with a bias of −10.00 V. A Sony HADCCD11 camera was positioned directly in front of the cell (135 mm). A Ref-600 potentiostat (Gamry) operated in chronoanopmerometry mode at 3 V. Potentiostatic operation was selected to avoid side reactions on the ITO and ensure system longevity. Once purged with water the cell was filled with electrolyte solution at 11 mL min⁻¹. For RFB experiments, performance curves were captured using a 857 RFC Test System (Scribner Associates) with cell voltages iR corrected using the simultaneously determined high frequency resistance (HFR).

Fig. 1. (A) Experimental set-up for ECL experiments. (B) Description of different ECL reactor operation modes: absence of porous media; (C) with electrochemically inactive porous media and (D) with active porous electrode.
independent compartments separated by a Nafton membrane. For that purpose, polarization curves as a function of electrolyte flow rate and FF design were measured with a 100%-charged 0.3 M VOSO$_4$ in 0.6 M H$_2$SO$_4$. This electrolyte formulation has a lower concentration of active species and supporting electrolyte than standard vanadium RFBs and was selected to enhance transport limitations responsible for our experimental results. Fig. 2C shows the IR-free curves for the interdigitated FF between 0 and 100 mL min$^{-1}$ with ohmic resistance shown as inset. Non-activated carbon paper electrodes was used for these experiments which led to a very linear shape of the I$^e$V curves most likely due to poor catalytic activity. Fig. 2D shows the current density achieved with battery discharge at 0.4 V. At this potential and based on the moderate electrolyte concentration, the system is significantly affected by mass transport—increasing flow directly increases battery performance. Interestingly the trend of photocurrent shown in Fig. 1B and battery current density in Fig. 1D are very similar (see inset in Fig. 2(D) for comparison).

Indeed, both experiments with similar cell design show 3–4 higher current density and measured photocurrent with the interdigitated design. Divergence in the trend between both experimental set-ups (ECL-reactor and RFB), could be linked to different concentration & diffusion coefficients of active species, and different electrolyte viscosities. However, the consistency of our observations supports our analogy between luminol reactant distribution and light emission with the investigation of processes occurring in real RFBs.

As a consequence we decided to investigate frames taken from the recordings and their corresponding pixel light intensity to establish a correlation between local concentration on the electrode and light intensity (Videos corresponding to the experiments in Fig. 3(A) & (B) can be viewed [23]). This allows us to study the mass transport phenomena under different conditions and at different points through the FF. Fig. 3(A) & (B) shows that the FF patterns are observed when just a planar electrode was employed. This response is associated with the small distance between the ITO electrode and the FF leading to reactant starvation under the lands and an increased iR drop in this region.

The observation of the frames allowed us to see dead-ended regions in the Interdigitated FF where little reaction occurs due to incomplete wetting. There are also regions in both FFs where reaction is blocked in the channel due to gas bubbles, but in the serpentine flow these bubbles are seen to flow through the system and out (see videos [23]). In interdigitated systems, the bubbles remain at the end of the dead ended channels and contribute to regions with low reactivity. Promotion of turbulent flow due to flow direction change is in agreement with mathematical modelling of serpentine FFs [9].

When comparing both FFs, a more homogenous distribution of reactant is found for the serpentine. Significantly larger photocurrents were observed for the interdigitated FF associated with a design that forces the electrolyte towards the planar electrode and which causes higher pixel intensity at areas closer to liquid inlet and outlet. In an RFB, this design leads to higher current density. However, as discussed by Houser et al. a non-homogenous reactant distribution would be observed leading to uneven current distribution which due to ohmic drop may enhance the degradation of the electrode [15]. Besides that, the interdigitated design would lead to a larger electrolyte pressure drop, and hence parasitic pumping loses.

Understanding the electrolyte/electrode interaction with carbon paper electrodes is important as these improved materials have demonstrated high power density in all-vanadium RFBs [24]. We studied
convective reactant transport in the RFB using SGL carbon paper. This allowed us to visualize transport through tortuous materials. For this purpose, the carbon material was placed in direct contact with the ITO electrode and the FF (sandwiched between them). As previously observed, the ECL reaction provides light emission which imitates the shape of the FF (Fig. 3C). Under these circumstances the overlapping of carbon fibres blocks much of the light as the majority of reaction takes place on the electrode face adjacent to the flow channel, depleting reactant within the body of the carbon material. This is supported by experiments using electrochemically inactive tortuous materials (Fig. 3D). The reaction of luminol after crossing the glass fibre paper produces a light distribution which does not follow the FF. Integration of all pixels reveals greater reaction rates in areas close to the electrolyte inlet which suggests our ECL method may be used to investigate microstructural effects such as the competition between preferential in-plane wetting/permeation over through-plane electrolyte transport. For an RFB electrode a similar effect is observed with slightly higher pixel intensity closer to the electrolyte inlet and outlet which may be associated with electrolyte bypass (i.e. the electrolyte does not flow through the channels but passes directly from inlet to outlet). The impact of electrolyte bypass in a RFB could therefore be minimized by simply placing electrolyte inlet and outlet opposite to each other. A future evolution of our technique may be used to identify catalytic centres within the electrochemically active material utilising microscopy.

4. Conclusion

We present an ECL-based electrochemical cell in which light emission and intensity can be utilised to track RFB performance. We utilised camera recordings and photodiode light detection for different electrolyte formulations (concentration and flow) in order to validate our method. This allowed us to correlate spatial light emission patterns for different FF designs with mass transport phenomena and compare these to real all-vanadium RFB performance. We investigated liquid electrolyte transport though both electrochemically inactive and active tortuous materials and demonstrated that electrolyte bypass associated might be an important transport mechanism.

Acknowledgements

This work was funded by the UK EPSRC project “Energy Storage for Low Carbon Grids” (EP/K002252/1). Data for figures are available [25].
References

[1] A.Z. Weber, M.M. Mench, J.P. Meyers, P.N. Ross, J.T. Gostick, Q. Liu, Redox flow batteries: a review, J. Appl. Electrochem. 41 (2011) 1137–1164.

[2] M. Govindan, K. He, I.-S. Moon, Evaluation of dual electrochemical cell design for cerium-vanadium redox flow battery to use different combination of electrodes, Int. J. Electrochem. Sci. 8 (2013) 10265-10279.

[3] Z. Siroma, S.-i. Yamazaki, N. Fujiwara, M. Asahi, T. Nagai, T. Ioroi, Indirect fuel cell based on a redox-flow battery with a new design to avoid crossover, J. Power Sources 242 (2013) 106–113.

[4] A.K.-y. Yoon, H. Choe, Y.S. Yoon, Design and test of a lab-scale vanadium redox flow battery considering electrolyte feeding structure for solar energy, in: G. Yang (Ed.), Materials Science, Machinery and Energy Engineering, vol. 853, 2014, pp. 291–296.

[5] C. Flox, M. Skoumal, J. Rubio-Garcia, T. Andreu, J. Ramon Morante, Strategies for enhancing electrochemical activity of carbon-based electrodes for all-vanadium redox flow batteries, Appl. Energy 109 (2013) 344–351.

[6] C. Flox, J. Rubio-Garcia, R. Nafria, R. Zamani, M. Skoumal, T. Andreu, A. Arbiol, A. Cabot, I. Ramon Morante, Active nano-CuP3 electrocatalyst supported on graphene for enhancing reactions at the cathode in all-vanadium redox flow batteries, Carbon 50 (2012) 2372–2374.

[7] C. Flox, J. Rubio-Garcia, M. Skoumal, T. Andreu, J. Ramon Morante, Thermo-chemical treatments based on NH3/O2 for improved graphite-based fiber electrodes in vanadium redox flow batteries, Carbon 60 (2013) 280–288.

[8] C. Flox, J. Rubio-Garcia, M. Skoumal, J. Vazquez-Galvan, E. Ventosa, J.R. Morante, Thermally stable positive electrolytes with a superior performance in all-vanadium redox flow batteries, Chem. Aust. 80 (2015) 354–358.

[9] Q. Xu, T.S. Zhao, P.K. Leung, Numerical investigations of flow field designs for vanadium redox flow batteries, Appl. Energy 105 (2013) 47–56.

[10] D. Aaron, Z. Tang, A.B. Papandrew, T.A. Zawodzinski, Polarization curve analysis of all-vanadium redox flow batteries, J. Appl. Electrochem. 41 (2011) 1175–1182.

[11] C. Kalvys, A. Kucernak, D. Brett, G. Hinds, S. Atkins, N. Brandson, Spatially resolved diagnostic methods for polymer electrolyte fuel cells: a review, Wiley Interdiscip. Rev. Energy Environ. 3 (2014) 254–275.

[12] M.H. Wang, H. Guo, C.F. Ma, Temperature distribution on the MEA surface of a PEMFC with serpentine channel flow bed, J. Power Sources 157 (2006) 181–187.

[13] S. Tsushima, K. Teranishi, K. Nishida, S. Hirai, Water content distribution in a polymer electrolyte membrane for advanced fuel cell system with liquid water supply, Magn. Reson. Imaging 23 (2005) 255–258.

[14] R.J. Bellows, M.Y. Lin, M. Arif, A.K. Thompson, D. Jacobson, Neutron imaging technique for in situ measurement of water transport gradients within Nafion in polymer electrolyte fuel cells, J. Electrochem. Soc. 146 (1999) 1099–1103.

[15] J. Houser, J. Clement, A. Pezeshki, M.M. Mench, Influence of architecture and material properties on vanadium redox flow battery performance, J. Power Sources 302 (2016) 369–377.

[16] A.A. Wang, M.J. Aziz, S. Rubinstein, Direct visualization of electrochemical reactions and comparison of commercial carbon papers in operando by fluorescence microscopy using a quinone-based flow cell, ECS Trans. 77 (2017) 153–161.

[17] T. Lopes, M. Ho, B.K. Kakati, A.R.J. Kucernak, Assessing the performance of reactant transport layers and flow fields towards oxygen transport: a new imaging method based on chemiluminescence, J. Power Sources 274 (2015) 382–392.

[18] O. Beruski, T. Lopes, A.R.J. Kucernak, J. Perez, Investigation of convective transport in the gas diffusion layer used in polymer electrolyte fuel cells, Phys. Rev. Fluids 2 (2017).

[19] S. Sakurai, Electrochemiluminescence of hydrogen-peroxide luminol at a carbon electrode, Anal. Chim. Acta 262 (1992) 49–57.

[20] P. Biparva, S.M. Abedirad, S.Y. Kazemi, ZnO nanoparticles as an oxidase mimic-mediated flow-injection chemiluminescence system for sensitive determination of carvedilol, Talanta 130 (2014) 116–121.

[21] R.C. Engstrom, K.W. Johnson, S. Desjarlais, Characterization of electrode heterogeneity with electrogenerated chemiluminescence, Anal. Chem. 59 (1987) 670–673.

[22] L. Zhu, Y.X. Li, G.Y. Zhu, A novel flow through optical fiber biosensor for glucose based on luminol electrochemiluminescence, Sensors Actuators B Chem. 86 (2002) 209–214.

[23] J. Rubio-Garcia, A. Kucernak, Videos of Electrochemiluminescence Response for Paper “Direct Visualization of Reactant Transport in Forced Convection Electrochemical Cells and Its Application to Redox Flow Batteries”, (2018), http://dx.doi.org/10.5281/zenodo.1294714.

[24] Q.H. Liu, G.M. Grim, A.B. Papandrew, A. Turhan, T.A. Zawodzinski, M.M. Mench, High performance vanadium redox flow batteries with optimized electrode configuration and membrane selection, J. Electrochem. Soc. 159 (2012) A1246–A1252.

[25] J. Rubio-Garcia, A. Kucernak, Data Used for Figures in Paper “Direct Visualization of Reactant Transport in Forced Convection Electrochemical Cells and Its Application to Redox Flow Batteries”, (2018), http://dx.doi.org/10.5281/zenodo.1304914.