

Electrochemical Study of the Bromide/Bromine Reaction in Nonaqueous Solvents

Brent Bennett^a, Jinho Chang^b, and Allen J. Bard^{a,b}

^aMaterials Science and Engineering Graduate Program
The University of Texas at Austin
Austin, TX 78712, USA

^bDepartment of Chemistry and Biochemistry
The University of Texas at Austin
Austin, TX 78712, USA

Nonaqueous solvents offer the potential to create redox flow batteries (RFBs) with higher energy densities, new cell designs, and cheaper materials. Incorporating all of these advantages could lead to the creation of flow batteries with much lower capital costs, which is the primary factor preventing their commercialization. Therefore, interest in nonaqueous solvents for redox flow batteries has grown in recent years [1]. With these advantages in mind, the Bard group has begun investigating the use of the bromide/bromine (Br^-/Br_2) redox couple as a positive electrode in nonaqueous solvents.

The Br^-/Br_2 redox couple has a large positive redox potential (~ 1 V vs. NHE), a two-electron transfer, and high solubility in many solvents. In aqueous systems, Br^-/Br_2 is an efficient and reversible reaction. Hence, it has been the subject of much study for RFBs and has found a commercial application in the zinc/bromine flow battery [2]. However, in most nonaqueous solvents, this reaction is a complex two-part process through a stable tribromide ion intermediate and is highly irreversible (see Figure 1). Although this reaction has been investigated for over 50 years in solvents such as acetonitrile [3], no consensus has been reached on the reaction mechanism beyond that point. In order to better understand how we can use this redox couple in a RFB, we have decided to study the mechanism in detail.

Our initial investigation of the oxidation of bromide to tribromide, using fast-scan cyclic voltammetry and scanning electrochemical microscopy (SECM), has revealed that an adsorbed bromine radical (Br_2^-) is an intermediate product in this reaction. This finding suggests that the reaction mechanism follows an ECC pattern, in which the first oxidation step is followed by the addition of a bromide ion to form the Br_2^- radical before forming tribromide. We have also found evidence of a different intermediate during the reduction of tribromide to bromide, suggesting that the reduction follows an ECEC mechanism. No previous studies of the Br^-/Br_2 reaction in nonaqueous solvents

have provided evidence of these intermediates nor has any study been attempted to discover the elementary reaction steps that make up the complete reaction.

In the near future, we intend to fully characterize the reaction steps between bromide and tribromide and to use these same techniques to investigate the oxidation of tribromide to bromine, which is the second step of the bromide/bromine reaction. Once we gain a full understanding of the reaction mechanism, we hope to create prototype flow cells using tribromide/bromine as the positive electrode in a nonaqueous solvent.

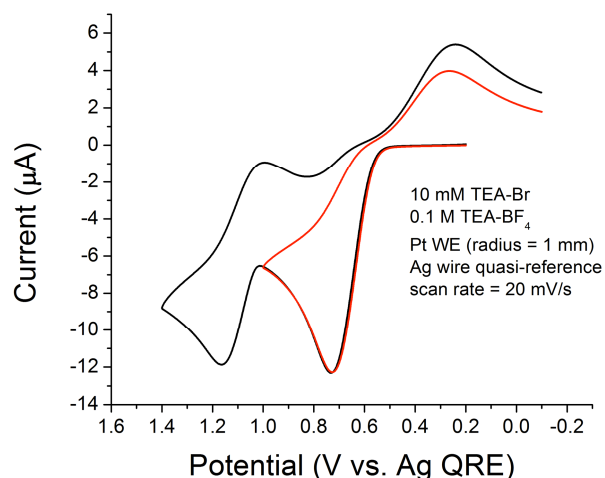


Figure 1: Cyclic voltammogram of the bromide/bromine redox couple in nitrobenzene.

References:

- [1] S.-H. Shin, S.-H. Yun, and S.-H. Moon, "A review of current developments in non-aqueous redox flow batteries: characterization of their membranes for design perspective," *RSC Adv.*, 2013, Advance Article.
- [2] ZBB Energy Corporation, <http://www.zbbenergy.com/>
- [3] A.I. Popov and D.H. Geske, "Studies on the Chemistry of Halogen and of Polyhalides. XVI. Voltammetry of Bromine and Interhalogen Species in Acetonitrile", *J. Am. Chem. Soc.*, **80**, 5346 (1958).