



Research Paper

In situ Confocal Microscopy of Electrochemical Generation and Collision of Emulsion Droplets in Bromide Redox System



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ABSTRACT

For redox flow battery, 1-ethyl-1-methylpyrrolidinium bromide (MEPBr) is a promising bromine-complexing agent that forms insoluble organic phase of MEPBr₃. A series of optical images acquired by *in-situ* confocal microscopy with tens of millisecond interval visualize how MEPBr₃ emulsion droplets are electrochemically generated and collide with the electrode surface. Two types of electrodes, i.e. a Pt microdisk of 10 μm diameter and a 2.5 mm long Pt wire of 25 μm diameter, show clear correlation between electrochemical behavior and optical images. The droplets starts growing on the electrode surface at the potential at which oxidative faradaic current starts flowing. As the overpotential increases, the droplets become larger adhered at the electrode surface, from which small droplets start detaching at 0.925 V or higher potential. Some of the droplets leave the surface, move back and collide with the electrode surface, thus producing current spikes, which are detected by chronoamperometry simultaneously. *In-situ* confocal microscopy in this study confirms that the droplets are heterogeneously generated by electrochemical reaction and that individual droplets collide back onto the electrode surface, thus providing a better understanding of the phenomena that happen at redox flow battery electrode surfaces.

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1. Introduction

Emulsion droplets have been an interesting research theme for various aspects in industrial processes. What we can access to investigate droplets is mostly ensemble properties. Lack of proper analytical methods to characterize individual particles is the cause of such limited knowledge about them. In this regard, 'particle-impact chronoamperometry' is getting a new spotlight recently [1,2]. This technique is a simple but informative way to detect electrochemical signals originated by individual particles [1]. In the presence of particles near the electrode, chronoamperometry typically gives current spikes [3], which are current surges that happen when the particles contact the electrode surface [2]. Such current spikes contain information about size [3], concentration

[4], and aggregation state [5] of the particles and electron transfer associated with them [6–8]. This method is applied to study of, not only metal nanoparticles but also 'soft particles', such as liposomes [9–12], viruses [13], single macromolecules [14] and emulsion droplets containing redox species [15–17].

1-ethyl-1-methylpyrrolidinium bromide (MEPBr) is one of quaternary ammonium bromides (QBr's) widely used in redox flow batteries (RFBs) [18–21]. It captures electrochemically produced bromine (Br₂), during electro-oxidation of Br⁻, to induce the formation of insoluble organic emulsion droplets of MEPBr₃. Formation of such emulsion prevents from permeation through the battery membrane and self-discharging of electrogenerated Br₂, which is one of the key causes bringing about malfunction of RFB systems [22–28]. Reportedly, MEPBr₃ droplets participate in Br⁻ electrooxidation rather than behaving merely as bromine complexing agents [29], making the system even more complex. The electrochemistry involving MEPBr and MEPBr₃, however, remains unknown. For instance, it is uncertain whether the MEPBr₃ emulsions are homogeneously created in aqueous solution or heterogeneously formed on the Pt electrode. There has been few

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previous study on movement and behavior of electrochemically generated MEPBr₃ emulsion as a function of time. The recent simulation work reported a model based on the assumption of static geometry, telling little concerning dynamic emulsion. [29,31] In addition, it is still unclear what causes the characteristic spikes in chronoamperograms, requiring lack of direct experimental evidence. It is also unknown why the oxidative current of MEPBr is larger than currents from aqueous Br⁻ oxidation without MEP⁺.

In this study, we investigate the electro-oxidation of Br⁻ in MEPBr₃ droplet through comparison between electrochemical analysis and *in-situ* confocal microscopy. Previous reports showed collision events of particles such as nanoparticles, fluorescent beads and some soft particles through fluorescence [30,31] and plasmonic signals [32–36] that are produced when particles collide with the electrode. Unfortunately, it is difficult to directly observe the generation and behavior of particles in the solution. This led us to seek an alternative way of observing the MEPBr₃ droplets, i.e. by using *in-situ* confocal microscopy. Droplets are predicted to be a few μm in diameter, for which confocal microscopy can provide direct optical images with sufficient resolution. The optical images can show the change in droplets at the focused range used. Using cylindrical wire electrode helps with monitoring the stereoscopic movement of droplet and ultramicroelectrode (UME) giving low background current suits for simultaneous acquisition of the optical images and transient current caused by a droplet collision moment. Therefore, *in-situ* confocal microscopy allows us to see directly generation, diffusion, and collision of the droplets at the electrode, and how they change as potential varies. These are expected to provide a better understanding of the contribution of MEPBr₃ droplets to the oxidation of Br⁻ in redox flow batteries.

2. Experimental

2.1. Materials and reagents

1-ethyl-1-methylpyrrolidinium bromide and potassium bromide were acquired from Sigma-Aldrich. Sulfuric acid (95%) and potassium sulfate were purchased from Deajung and Alfa Aesar, respectively. All the aqueous solutions in these experiments were prepared with ultrapure deionized water produced by a Barnstead Nanopure system from Thermo Scientific.

2.2. Electrochemical measurements

Cyclic voltammograms and chronoamperograms were obtained with a CHI 750 electrochemical workstation from CHI instruments. The electrochemical cell consisted of three

electrodes. The working electrodes were either a Pt UMEs (diameter: $d = 10 \mu\text{m}$) or a Pt microwire electrode (diameter: $d = 25 \mu\text{m}$). A silver/silver chloride (3 M potassium chloride) and a Pt wire were used as reference and counter electrode, respectively. The pH of the solutions comprising 0.5 M potassium sulfate and 1-ethyl-1-methylpyrrolidinium bromide or potassium bromide, was adjusted with sulfuric acid.

2.3. Confocal microscopy imaging

Imaging was carried out with a Zeiss LSM880 confocal laser scanning microscope equipped with a laser argon-multiline for RGB and a water-immersion objective (20x, N.A. = 1.0; Zeiss). Series of images were acquired with the interval of about 15 ~ 150 ms and were sharpened to clearly see the shape and movement of the droplet using a ZEN (black edition; Zeiss) software.

3. Results and discussion

The homogeneous complexation process of MEPBr₃ proposed in the literature is represented as follows [29].



This suggested mechanism proposes that Br₃⁻, which is generated on the electrode surface in reaction (1), encounters the 1-ethyl-1-methylpyrrolidinium cation, MEP⁺, to form a complex homogeneously, MEPBr₃, as described in reaction (2). This is supported by *in-situ* FT-IR investigations [26,27]. Multiple insoluble MEPBr₃ complexes agglomerate themselves to create a droplet in the aqueous solution. When the droplet hanging around the solution happens to reach the electrode surface, additional spike current is produced in voltammograms and chronoamperograms. From the electrochemical analysis and simulation study in MEPBr₃ droplet, it was predicted that Br⁻ is enriched *ca.* 7.5 M in the droplet and causes the spike current. [29,37]. This is a proposed scenario, although highly probable as implied by a couple of indirect observations, which has not been proved by direct imaging and thereby the respective steps of the previously mentioned mechanism remains veiled to date.

To address this issue, we introduce confocal microscopy to monitor what occurs at the electrode during the electrochemical measurements. Fig. 1 shows the experimental scheme for simultaneous measurements using a potentiostat and a confocal microscope. Three electrodes, including a Pt wire or a UME as working electrodes, constitute the electrochemical system

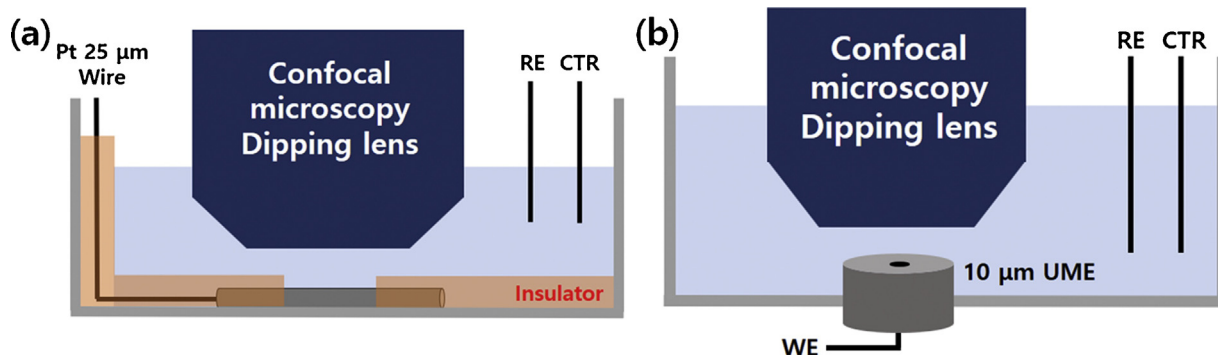


Fig. 1. Schematic diagram of electrochemical measurement and confocal imaging. (a) Pt wire (25 μm in diameter) insulated except the part exposed to the electrolyte (*ca.* 2.5 mm long) (b) Pt UME (10 μm in diameter) utilized in electrochemical cell.

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