Enhanced vanadium redox flow battery performance using graphene nanoplatelets to decorate carbon electrodes

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HIGHLIGHTS

- Electrostatic assembly is used to decorate electrodes with graphene nanoplatelets.
- Significant enhancement of VO^{2+}/VO_2^+ redox kinetics with number of layers.
- Tafel slope and edge site density increase with number of layers.
- Decoration of carbon felt (CF) enhances operating battery performance.

GRAPHICAL ABSTRACT
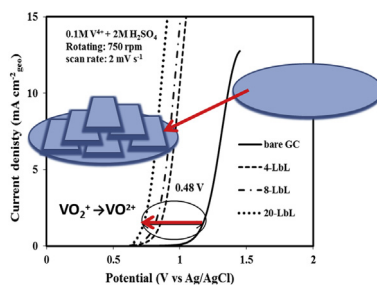
ABSTRACT

Rotating Disk Electrode (RDE) measurements on model glassy carbon (GC) substrates and Cyclic Voltammetry on more practical commercial carbon supports are used to demonstrate that the kinetics of the positive VO^{2+}/VO_2^+ redox reaction can be substantially enhanced by using electrostatic layer-by-layer assembly (LbL) to decorate their surface with graphene nanoplatelets (GNPs). An exchange current density, i_0, is obtained that is more than two orders of magnitude greater than that observed with standard carbon supported Pt nanocatalyst with the deposition of only 20 GNP layers. Tafel slope analysis is compared to electron microscopy imaging to conclude that while faster redox kinetics is associated with an increase in the available active area, the prevalence of smaller GNPs and associated edge sites the can attenuate activity gains with increasing number of layers. Practical implementation to existing Vanadium Redox Flow Battery (VRFB) configurations was demonstrated through the application of a 370 nm (20 layer) LbL GNP coating on carbon felt (CF). The GNP coating yielded a 5% increase relative in voltage and overall efficiency of charge discharge curves obtained under typical VRFB cell operating conditions at $40 \, mA \, cm^{-2}$. Furthermore, a substantial increase in the discharge time is observed with this GNP coating on CF.

1. Introduction

Wide incorporation of renewable solar and wind energy into the commercial energy grid requires development of large-scale energy storage systems that attenuate the intermittent nature of these power sources. Among the most promising candidates for electrochemical energy conversion and storage technologies at the grid-level is the vanadium redox flow battery (VRFB) [1,2]. The advantage of a flow system over a conventional solid state battery approach is that energy (kWh) and power (kW) are decoupled and can be sized for any given

application. Furthermore, the ability of vanadium to exist in solution in four different oxidation states permits use of the same species as the anolyte and catholyte, overcoming a major issue of cross-contamination observed in other flow battery systems. However, the high cost of stack materials drives continuing efforts increase the power density of each cell. Toward this end, significant research has gone into understanding and enhancing the electrocatalytic activity of VRFB electrode materials. Allotropes of carbon are ideal electrocatalyst candidates for VRFB applications due to their low cost, high chemical stability and wide potential window for operation [3,4]. These materials can be used to exploit a classic strategy in electrocatalysis whereby power density is increased by increasing the available active area per unit volume. Hence, carbon felt (CF), carbon fibers and graphitized carbon papers have been investigated as practical substrates due their porous, three-dimensional conductive structures, electrochemical stability and very large surface area [5–7]. More recently, nanoscale carbon materials such as single-walled and multi-walled carbon nanotubes (SWCNTs and MWCNTs) [8,9], carbon nanowires (CNW) and carbon nanofibers (CNF) [10], and GNPs [11,12] have gained attention due to the realization of large surface areas. Along with classic surface area enhancement, the surface chemistry of carbon materials has been used to influence the intrinsic vanadium redox reaction kinetics and thus various methods of surface chemical modification have been explored. For example, chemical and heat treatments have enhanced electrochemical activity of carbon through surface hydroxylation that increases the concentration of surface active groups (C-O, -OH and –COOH groups) [13,14]. The incorporation of metal electrocatalysts onto carbon surface has also been investigated [9,15,16]. The decoration of CF by carbon nanotubes has also been shown to improve electrocatalytic activity and battery performance [17]. Nafion was used as binder and the nanoplatelets deposited randomly on the surface of CF through dip-coating. In our investigation, we examine the use of electrostatic Layer-by-Layer (LbL) assembly to decorate the surfaces of both practical carbon substrates such as CF as well as model glassy carbon (GC) substrates with graphene nanoplatelets (GNPs). LbL assembly of the GNPs has been previously shown to yield a more controlled morphology [18–20] than a dip-coating process and will be in this paper shown to provide improved structure-property correlation to electrocatalytic activity.

The VO^{2+}/VO_2^+ and V^{3+}/V^{2+} redox reactions on typical carbon surfaces have been attributed to the binding of vanadium species to surface oxygen groups followed by an electron transfer and the subsequent desorption of the vanadium ion [13,21]. The bound vanadium species is also capable of acting as an active site to transfer electrons to other adjacent vanadium species [22,23]. The orientation of the basal and edge-sites of the graphite structure, with edge sites possessing a higher surface density of oxygen-containing functional groups relative basal planes, will largely influence the charge transfer polarization during operation. It is understood from previous studies that the edge and basal planes of carbon exhibit different responses to faradaic and non-faradaic processes and have an influence in the redox kinetics for VRFB reactions [24,25]. Developing a technique to apply GNP's in a well-controlled manner is the logical next step in order to realize the full potential of these materials [26].

LbL assembly of both organic and inorganic nanoparticles (NPs) is a simple and elegant technique that has gained much attention since its introduction by Iler a number of years ago [27]. The technique provides a versatile approach for creating functionalized multilayer structures from nanoparticle suspensions. Assembly occurs primarily through strong electrostatic bonding allowing for different types of charged materials to be deposited in a uniform manner. However, LbL assembly has rarely been applied to fabricate macroscopic electrodes. The chief reason for this is that metal nanoparticles typically used as electrocatalysts do not contain native (i.e., covalently bonded) surface charges that can be exploited for electrostatic assembly. Not surprisingly, attempts at LbL assembly with Pt NPs synthesized utilizing standard methods have yielded very poor metal uptake and correspondingly low activity [28]. By contrast, our own group has more recently shown that Pt NPs deliberately synthesized to contain inorganic surface ligands with a strong negative charge can be readily assembled into well-defined layered structures that yield enhanced electrocatalytic activity in fuel cell applications [29–31]. Carbon NPs also possess native electrostatic charges on their surface through dissociation of carboxylic and phenolic groups at the appropriate pH to form –COO⁻ and –O⁻ moieties. Despite the potential for electrostatic LbL assembly of carbon NPs to fabricate macroscopic electrodes with well-defined nanostructures, a study has yet to appear utilizing such an approach.

While seldom used for electrode fabrication, electrostatic LbL assembly of carbon NPs has been widely realized in fields ranging from perm-selective membranes to solid-state batteries and supercapacitors [32–35]. In our own lab, we have previously shown the use of this technique to produce electrically conductive coatings with well-defined surface wettability for application in proton exchange membrane (PEM) fuel cells. A cationic polyelectrolyte typically used to provide the opposing charge for LbL assembly of carbon NPs and adopts an expanded chain conformation upon adsorption. Consequently, unlike polymeric binder used in polymer composite materials prepared by, for example, dip-coating, a substantial portion of the underlying material remains exposed. Negligible increase in the contact resistance is therefore observed due to the presence of polyelectrolyte [18–20].

In the present work, we investigate LbL assembly of GNPs to fabricate electrodes used for the VO^{2+}/VO_2^+ redox reaction in VRFBs. LbL assembly has been previously employed in VRFB applications to develop novel composite membranes to minimize self-discharge and the crossover of vanadium species during operation [35]. In the case of electrodes, LbL assembly technique can be highly suitable for thin-film uniform deposition on carbon papers and CF. Apart from fine structure control to enhance surface area and activity, electrostatic assembly is well-suited to commercial micro-fluidic RFB fabrication as it provides a convenient method to produce conformal coatings on the fine channels of bipolar plates (BPs). We here report the use of electrostatic LbL assembly technique to deposit commercially available GNPs from stable suspensions, using a strong cationic polyelectrolyte, onto carbon electrodes ranging from GC for fundamental investigation to BP used in the construction of microfluidic cells and finally to CF used in practical VRFBs. We identify the fundamental mechanisms behind the observed electrochemical activity of these structures using Rotating Disk Electrode (RDE) and Cyclic Voltammetry (CV) analysis on GC supports. We also present data on the creation of multilayer assemblies of up to 100 nanoparticle layers on commercially available GBP substrates and analyze mass-normalized performance using voltammetry and Electrochemical Impedance Spectroscopy (EIS). Finally, we show how LbL assembly of GNPs greatly enhances the kinetics of the positive VO^{2+}/VO_2^+ redox chemistry relative to comparably thick alternate carbon structures such as CF.

2. Materials and methods

2.1. Graphene nanoplatelets

GNPs have been previously shown to improve the electrocatalytic properties for VRFB systems [11,12]. GNPs exhibit excellent catalytic activity due to a very high electronic conductivity network and the location of surface oxygen edge-defects which is tunable by functionalization methods. The GNPs used in this study were obtained in the form of a paste (Aquadag-E from Ladd Laboratories). This material has been used as a conductive coating for cathode ray tube applications. However, in our study, the GNPs are dispersed as a stable colloidal suspension at the desired pH. The surface charge of the GNPs is altered by varying the pH. The GNPs in Aquadag E have been characterized extensively in our previous investigations [18–20]. The platelets have a relatively uniform thickness ranging between 5 and 10 nm and highly