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Review Article

Graphene oxide membranes for electrochemical energy storage and conversion

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ABSTRACT

Graphene oxide (GO) membranes have recently attracted considerable attention for various applications involving filtration. In electrochemical systems, GO membranes serve as a separator or solid-state electrolyte; the roles which have been played for over four decades by the commercial ionic polymers such as Nafion. Owing to the versatility of GO membranes, they have shown an incredible potential for electrochemical energy storage and conversion. In lithium-sulphur batteries and similar electrochemical systems in which the electrode redox system is based on a conversion mechanism and subject to the so-called shuttle effect, a selective membrane can facilitate the transport of the electroactive species such as Li ions while blocking the release of the electroactive material (*e.g.*, polysulphides) into the other half-cell. The same requirement is essential for the fabrication of redox flow batteries. Owing to the growing interest in flexible supercapacitors, there is a desire to replace liquid electrolytes with solid electrolytes, and GO membrane provides an appropriate scaffold for trapping gel electrolytes. The performance of Nafion in fuel cells has also been improved by the preparation of GO/Nafion membranes. All these different applications reveal the practical potential of GO membranes for the future energy storage and conversion.

Contents

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Introduction

Since a common approach for the synthesis of graphene is exfoliation of graphite oxide, the subsequent reduction process is of utmost importance to prepare pure graphene [1–3]. However, the reduction is not complete, and this is the reason that the product is preferably called reduced graphene oxide (rGO) rather than graphene. There is indeed a wide range of materials between graphene oxide (GO) and rGO. The interaction of functional groups on the graphene surface provides a new opportunity for stacking the graphene layers in diverse arrangements as compared with the parallel stacking of graphite. This interaction, which is based on a collection of electrostatic forces, hydrogen bonding, hydrophilic interactions, etc, is indeed an alternative to the weak interactions between the π electrons in the graphite structure. The random stacking provides a unique feature to prepare flexible free-standing films, which is impossible to achieve with the graphitic architecture. In addition to mechanical flexibility, such films have appropriate porosity for the passage of small species (such as ions or small molecules). This is the reason that rGO and GO have been recently employed as membranes for a wide range of applications [4–10].

Depending on the membrane architecture and the chemical nature of the functional groups, GO membranes can be designed with desirable selectivity to the passage of specific species. For example, Nair et al. showed the capability of a GO membrane for filtering water while most of other liquids and gases were impermeable. This selectivity was attributed to the hydrophilicity of the corresponding membrane as well as the size of the sieve architecture [5]. In addition to the chemical composition, the permeability of GO membranes can be mechanically tuned [10]. Moreover, the moisture content can noticeably adjust the membrane performance [11]. In general, designing the GO membranes for various applications is now an active area of research.

Ionic polymers such as Nafion have been widely employed in the realm of electrochemistry during the past four decades [12–14]. These ionic polymers typically play two roles: separating the anode and cathode sides and/or serving as a solid electrolyte in all-solid-state cells. The former role has now become essential in the modern electrochemical energy storage devices due to the cell thinness to avoid an electrical shortcut, while the latter is becoming more popular for flexible power sources. Although various types of ionic polymer membranes are commercially available, they are still expensive for most applications. On the other hand, it is not easy to tune these membranes for specific applications. The majority of the research works employing ionic polymer membranes in electrochemical systems are based on commercial membranes. Hence, it is of both fundamental and practical interest to find novel membranes, which can be natively designed in a specific cell.

Inspired by the rapidly growing interest in GO membranes during the past year, the present work briefly reviews the advances in the GO applications as membranes for electrochemical energy storage and conversion.

Synthesis and properties

Graphite oxide

Graphite oxide has a long history, which backs to at least as early as the mid-nineteenth century. Despite a few synthesis routes devised, which are still among the main possible approaches for the preparation of graphite oxide, this mysterious material was not subject to active research until recent years. The recent attention is due to the possibility of utilising graphite oxide as a precursor for the preparation of graphene. However, the chemical structure of graphite oxide is still elusive. Ruoff and his workers reviewed possible chemical structures of graphite oxide [15].

Synthesis of graphite oxide is based on a basic scheme in which the carbon atoms are functionalised by various groups during an oxidation process. The key difference between various methods is the oxidising agent and the reaction environment. The oxidation process occurs within the graphite 2D interlayers where the interaction of the functional groups with the carbon atoms causes an expansion in the graphite interlayers. Changing the graphite stacking results in a visible change in the optical properties of graphite, as its colour changes from black/grey to a brownish spectrum. The final colour depends on the degree and type of oxidation.

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