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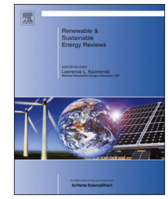

Graphene models and nano-scale characterization technologies for fuel cell vehicle electrodes

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A B S T R A C T

To address the demand for vehicles using fuel cell energy with high-performance electrodes, this paper discusses the energy storage model, nano-scale characterization technology, nanoenergy system and the structural design for fuel cell graphene electrodes while giving special attention to three characteristics: electrode conversion efficiency, specific power and cost. The structural stability model, evolutionary mechanism and the construction process of graphene electrodes of fuel cell technology are introduced. By analyzing electron and ion transmission and characterizing the electrode structure, energy system, surface and interface property at the nano-scale level, this paper reveals the intrinsic link between how an energy system is structured and performs. It combines the system model with the application of high-performance electrodes to highlight the compatibility between graphene and the electrode. By addressing progress in the applicability of renewable energy and the sustainability of energy technology during recent years, this paper provides scientific and experimental support for the practicality of fuel cell energy while also addressing bottleneck issues such as conversion efficiency, specific power and the cost of electrodes.

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1. Introduction

The increasing depletion of world oil reserves is a potentially fatal obstacle to providing perpetual energy for the world's vehicles. Moreover, the worsening environmental situation means that restrictions on vehicle emissions are becoming stricter [1,2]. It is therefore important to search for renewable and sustainable sources of vehicle energy. Traditional energy sources have reached a bottleneck stage, resulting in people changing their minds about these sources and turning to fuel cell vehicles instead. Water is the primary emission of fuel cell vehicles, which makes them an appealing alternative. The operation of fuel cell technology has no need for complex devices, lubricant, noise, or heat. The efficiency of fuel cell energy conversion is up to 36–69% [2]. Their high specific power means that fuel cells are renewable and sustainable, which defeats the shortage issue that exists when using traditional energy sources. Fuel cells cannot only overcome environmental challenges and energy supply problems, but they

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can also trigger a revolution in vehicle technology. Fuel cell electrodes, as the energy conversion and transmission channel, are rarely destroyed and have an extended life. However, there is still a significant amount of work to do before fuel cell vehicles will be able to compete with traditional vehicles. One job of particular importance is the need to reduce Pt as an electrode catalyst [3,4]. Decreasing costs and improving performance is also essential when studying possible new electrodes.

Fuel cell is the core of renewable and sustainable energy vehicles, of which electrode is vital in transforming sustainable energy into mechanical energy and heat, enabling vehicle motion and energy recovery. Renewable and sustainable energy vehicles require fuel cell to have high specific energy, high specific power, long mileage, and high speed, demanding electrodes to sustain instantaneously large current and high temperature under non-equilibrium and non-steady conditions [5]. At technical level, large current and high temperature frequently lead to nanostructure destruction, preventing electrode from achieving the expected performance and service life and threatening the security of energy storage devices. But security is one of the most important prerequisites for fuel cell technologies [6]. At scientific level, innovation of energy storage technology depends on the nano-scale performance of new energy electrode, stimulating related research work such as graphene energy system [3,6] and core–shell energy system [5,6].

Graphene can improve fuel cell performance and prolong its lifetime [5], which has attracted extensive concerns. Among energy storage devices used in renewable and sustainable energy vehicles, Li battery has high energy density, low specific power, but with long charging time [2,6], while supercapacitors have high specific power, low energy density, but with limited mileage [7]. Because of its high specific surface area, graphene fuel cell sheet forms on both sides an electric layer with wrinkles and pores that facilitate the proliferation of electrolyte. By meeting the requirements for specific energy and power, graphene electrode has broad prospects in the fields of fuel cell and fuel cells, with likely breakthrough achieved in the short term. For example, graphene composite electrode can offer excellent conductivity and improve the cycling performance. Its flexible and layered structure effectively inhibit the stress mutation and release of elastic energy due to volume changes in the fuel cell charge–discharge process and also extend the contact with collectors [6]. In addition, the use of graphene electrode as a conductive additive has greatly enhanced fuel cell's performance under large current, even outpacing carbon nanotube additives [7].

Graphene fuel cell overcomes the obstacles of low energy density and long charging time and accelerates the development of energy storage industry. However, nano energy storage defects in the process of charge–discharge cycles shall be eliminated before commercialization. In Nature 2012, winner of the Nobel Prize in Physics, Novoselov et al. [8] discussed about the potential applications of graphene in fuel cell, pointing out that mechanical stripping, vapor deposition, epitaxial growth, and solution-phase oxidation reduction cannot get defect-free fuel cell electrode, of which the morphology is even difficult to characterize. Graphene electrode does not dissolve easily and there are very limited techniques for assembly, design, and quantitative characterization at nano-scale [9]. Therefore, orderly arrangement and quantitative characterization of graphene nanostructure for high-quality electrode is a great challenge facing researchers in the fuel cell field.

2. Nano energy model of graphene fuel cell electrode structures under non-equilibrium state

Inside a fuel cell, hydrogen is inserted from an anode, and oxygen (or air) is inserted from a cathode. Electrolytes fill the space between the anode and cathode. A catalyst, Pt, helps hydrogen atoms split into protons and electrons, which reach the cathode to generate electric power and heat. Meanwhile, hydrogen and oxygen combine to once again form water. The structure of a fuel cell resembles a sandwich [10], as shown in Fig. 1a. However, the design of the electrodes and electronic circuits is complex. The rate of energy conversion and the speed of the vehicle is slow. In addition, Pt is needed as the catalyst, and this presents a problem because the auto industry's demand for Pt exceeds the global supply.

Therefore, a new electrode structure is needed to reduce or even eliminate Pt within a fuel cell while also enhancing the conversion and transmission of energy. In order to raise current density and reduce polarization, Shannon et al. [11] created an electrode with a porous, composite structure to enlarge the surface area of the electrode and allow the fuel cell to store increased charges, as shown in Fig. 1b. In this model, graphene electrodes are mounted in the form of a cross, similar to two fingers intersecting. This structure expands the available surface of the electrode and reduces the propagation distance for ions in the electrolyte. Porous fuel cells therefore have a greater charging capability than traditional cells.

When it comes to the extraction of protons and electrons, the reaction speed is proportional to the total surface area over which Pt particles make contact with the electrode. The smaller the Pt particles adhering to the electrode, the larger the total contact surface area is. Pt particles that have a diameter of 1–2 nm can be attached to graphene, which lead Eigler et al. to design a graphene multilayered electrode [12], as shown in Fig. 1c. In this design, the total contact area between the Pt particles and the electrode is increased. Pt particles move quickly between the nanostructure of graphene electrodes without accumulating carbon. This improves the utilization ratio, specific power, and catalytic activeness of hydrogen. Compared with traditional fuel cells, graphene electrodes use different mechanisms to store and release energy. Their unique two-dimensional structure results in a large surface area, high electrical conductivity and excellent physical properties. Therefore, the graphene electrode has significant potential in fuel cell technology and will undoubtedly become a major player in the fuel cell industry.

As the core component of fuel cell technology, the nanostructure of an electrode directly affects performance and cost. Graphene electrodes not only allow for the efficient transportation of molecules, ions and electrons, but they also improve catalyst utilization, control the degradation of the electrode and lower total cost. Therefore, the adjustment and control of the nanostructure of the graphene electrode and its evolutionary mechanism are crucial to electrode functions. Topics that need further study are the relationship between nanostructure and performance, nanoenergy systems and characterization methods. Xu et al. [13] took a single-layered graphene as a basic design and combined characterization technologies with system stimulation. Their design of a graphene electrode provides a scientific solution for performance improvement and cost reduction, as shown in Fig. 2a. Graphene is a dense layer of carbon atoms wrapped in a crystal lattice of honeycomb shape to form a novel two-dimensional atomic crystal. Its unit is the stable carbon hexagon inside the structure. Two-dimensional graphene crystal was first successfully obtained by Geim and Novoselov in 2004 at the University of Manchester, using micro-mechanical stripping method [9]. Published in the Science journal, their achievements won the 2010 Nobel Prize in Physics. Using SiC particles as a precursor and placing a metallic catalyst onto the graphene surface to act as an electrode, Suemisu et al. [14] measured the crystalline growth of the graphene structure vertically within the electrode system. They utilized a composite structure to hold the Pt and