Ball-Milling Used for the Preparation of Nitrogen-Doped Carbon-Based Electrocatalysts for the Oxygen Reduction Reaction

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The increase in the population and therefore, demand for the clean energy has forced the research to find efficient energy conversion technologies. Low-temperature fuel cell is a promising device that converts chemical energy into electrical energy, but since the oxygen reduction reaction (ORR) that takes place on the fuel cell’s cathode is quite slow, a good electrocatalyst is needed. Hereof, carbon-based materials (e.g. graphene, graphene oxide, graphite) have been widely used due to their low cost compared to metals, wide potential window in electrochemistry and mechanical stability [1]. However, it is known that the ORR on pristine carbon materials is rather inhibited, but heteroatom-doped carbon materials have shown great promise towards the ORR in alkaline media [1,2]. Many different but mostly complicated synthesis methods have been used for the preparation of heteroatom-doped carbon materials, but it is important to develop a catalyst material with high ORR activity, but using simple preparation method. In this regard, ball-milling is an attractive way for producing active catalysts towards the ORR since this method can be used for reducing the size of carbon materials but also for modifying the surface of nanocarbons [3,4].

In this work, carbon materials (graphite, graphene oxide or graphene) were ball-milled in the presence of dicyandiamide and then pyrolyzed at 800 °C to produce nitrogen-doped carbon material for the ORR in alkaline medium. The studies of high-resolution scanning electron microscopy and N\textsubscript{2} adsorption analysis showed that the ball-milling and nitrogen-doping changed the surface morphology and increased the specific surface area in graphite and graphene oxide, but no significant change was observed for N-doped graphene. According to the X-ray photoelectron spectroscopy analysis, the highest nitrogen content was found in N-doped graphite and the lowest in N-doped graphene. All these catalysts contained different nitrogen functionalities (amines, pyridinic-N and pyrrolic-N), but graphitic-N and pyridine-N-oxide was additionally detected in N-doped graphene [5].

All nitrogen-doped catalysts had higher electrocatalytic activity towards the ORR in alkaline medium compared to the undoped materials in terms of the number of electrons (\(n\)) transferred per O\textsubscript{2} molecule (for the N-doped materials the \(n\) value was ca four, but for the undoped ones it was between two and four) as well as the onset potential (e.g. the onset potential for the undoped and N-doped graphene oxide was -0.2 V and -0.05 V vs SCE, respectively). Inductively-coupled plasma mass spectrometry showed that only a small amount of Mn was found in N-doped graphene oxide, but not in N-doped graphite and N-doped graphene, so it can be assumed that the rise in electrocatalytic activity towards the oxygen reduction reaction is mostly associated with different nitrogen functionalities and the increase in the specific surface area after ball-milling. These results show that this simple and more environmentally-friendly method is suitable for the preparation of N-doped carbon-based catalysts for the ORR [5].

References