Dual-doped graphene/perovskite bifunctional catalysts and the oxygen reduction reaction

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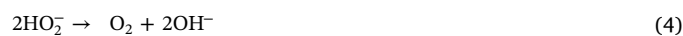
ABSTRACT

We report the first investigation of dual-doped graphene/perovskite mixtures as catalysts for oxygen reduction. Pairwise combinations of boron, nitrogen, phosphorus and sulfur precursors were co-reduced with graphene oxide and mixed with $La_{0.8}Sr_{0.2}MnO_3$ (LSM) to produce SN-Gr/LSM, PN-Gr/LSM and BN-Gr/LSM catalysts. In addition, the dual-doped graphenes, graphene, LSM, and commercial Pt/C were used as controls. The addition of LSM to the dual-doped graphenes significantly improved their catalytic performance, with optimised composition ratios enabling PN-Gr/LSM to achieve 85% of the current density of commercial Pt/C at − 0.6 V (vs. Ag/AgCl) at the same loading. The effective number of electrons increased to ca. 3.8, and kinetic analysis confirms the direct 4 electron pathway is favoured over the stepwise (2e + 2e) route: the rate of peroxide production was also found to be lowered by the addition of LSM to less than 10%.

1. Introduction

Research effort continues to focus on the oxygen reduction reaction (ORR) due to its importance in energy device applications (e.g., fuel cells and metal-air batteries) and, in particular, the search for more abundant and inexpensive catalyst replacements for the Pt-group materials is attracting increasing attention [1–3]. Amongst several candidates, perovskites have been demonstrated to be catalytically active [4–9]. However, the low conductivity typical of perovskites limits their application as single catalysts for the ORR [10].

In addition, graphene-related materials have also been considered due to its high conductivity and possibility of increasing the catalytic activity by the addition of dopant elements [11]. Specifically, dual-doped graphene with B, P or S in combination with N have been demonstrated to be catalytically active towards the oxygen reduction [12,13]. The combination of perovskites with highly conductive carbon materials have been previously reported for acetylene black [14], Vulcan carbon powder [15,16], Sibunit carbon [17], graphene [18,19], and even N-doped graphene [20,21], with varying results. The role of the carbon on the perovskite performance is still unclear. It has been proposed that the presence of carbon greatly improves the conductivity through the catalyst composite [22], whereas other workers suggest an influence of the carbon material on the ORR pathway [14,15]. In particular, the ORR can proceed in alkaline media via two different suggested mechanisms: either direct reduction of O_2 to OH^- by a 4-electron mechanism (Eq. (1)), or a 2-step process in which the O_2 is

partially reduced to peroxide in a 2-electron mechanism (Eq. (2)) followed by either further reduction to OH^- [Eq. (3)] or decomposition of peroxide (Eq. (4)) [23].

$$O_2 + 2H_2O + 4e^- \xrightarrow{k_1} 4OH^- \tag{1}$$

$$O_2 + H_2O + 2e^- \xrightarrow{k_2} HO_2^- + OH^- \tag{2}$$

$$HO_2^- + H_2O + 2e^- \xrightarrow{k_3} 3OH^- \tag{3}$$

$$2HO_2^- \rightarrow O_2 + 2OH^- \tag{4}$$

Here, we investigate combining dual-doped graphenes with a perovskite for the first time. These materials exhibit improved electrocatalytic activity due to the synergic effects of the dual-doped graphene/perovskite, and optimisation of the composition obtains the best performance in terms of both current densities and number of electrons transferred in the ORR yields results that approach that of Pt/C.

2. Experimental

The dual-doped graphene catalysts were prepared via a thermal annealing of a mixture formed by graphene oxide (GO, Nanoinnova Inc., prepared by Hummers method, impurities measured by XRF: 0.7% Mn, 0.05% Fe, 0.03% W, 0.02% Zn, 0.02% Cr), and the precursors of the different doping agents. These were: boric acid (Sigma Aldrich, ≥ 99.5%), melamine (Aldrich, 99%), orthophosphoric acid (Fisher
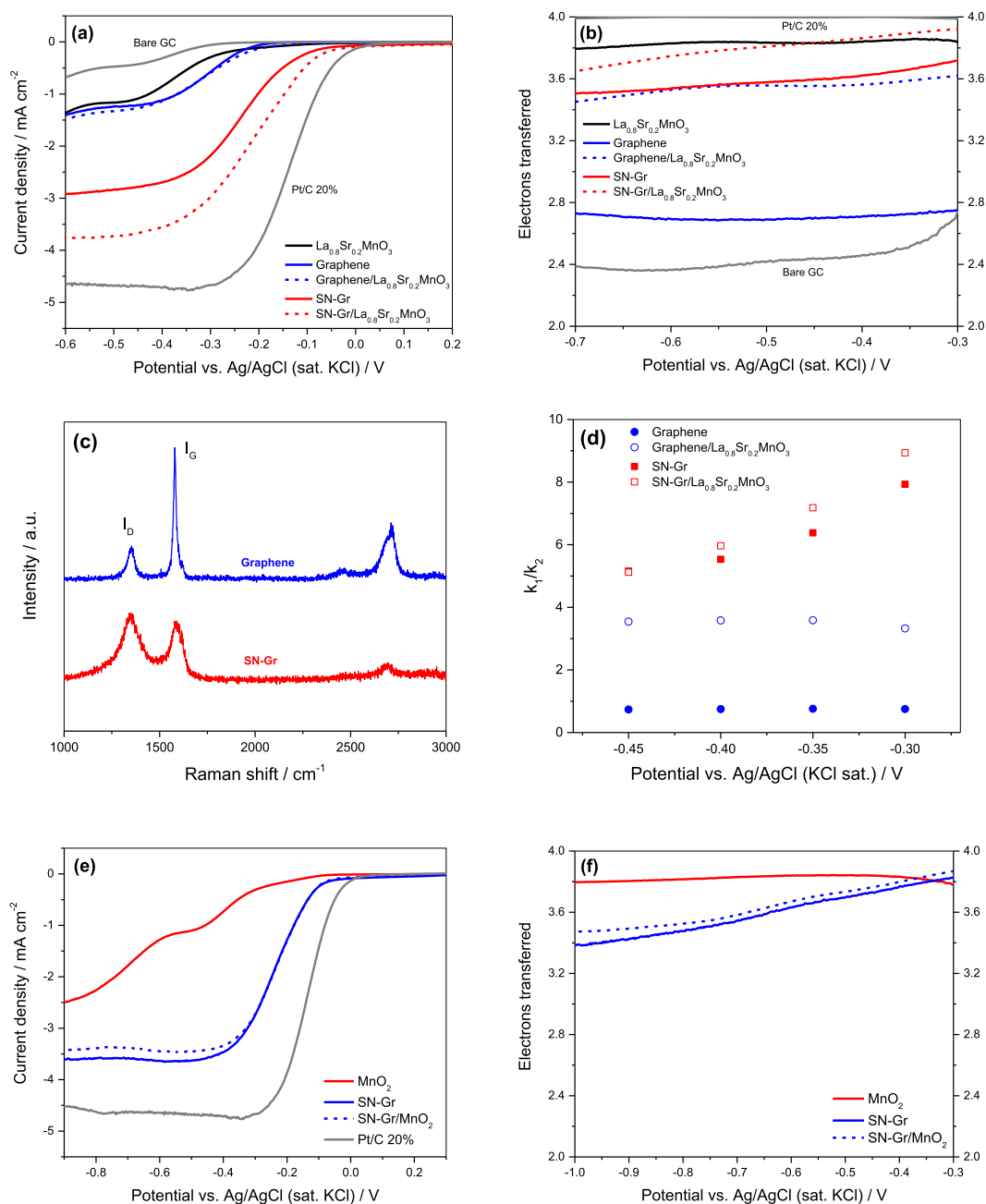
Fig. 1. (a) LSV of graphene and SN-Gr with and without perovskite in O_2-saturated 0.1 M KOH (measured at 10 mV s^{-1} scan rate and 1600 rpm, (doped)-graphene/LSM composites ratio 0.8:0.2, catalyst loading: 0.3 mg cm^{-2}). (b) Number of electrons transferred vs. potential obtained from RRDE measurements (ring potential fixed at + 0.5 V). (c) Raman spectra of pure graphene and SN-Gr. (d) k_1/k_2 ratios vs. potential (vs. sat. Ag/AgCl). (e) LSV of MnO_2, SN-Gr and combined SN-Gr/ MnO_2 in O_2-saturated 0.1 M KOH (measured at 10 mV s^{-1} scan rate and 1600 rpm, SN-Gr/MnO_2 composites ratio 0.8:0.2, catalyst loading: 0.4 mg cm^{-2}). (f) Number of electrons transferred vs. potential obtained from RRDE measurements (ring potential fixed at + 0.5 V).

Scientific, 86.75%) and dibenzyl disulfide (Aldrich, 98%). 100 mg of GO was mixed with 500 mg of melamine and 100 mg of the corresponding second precursor in 30 mL of ultrapure water (resistivity ≥ 18.2 MΩ cm, milli-Q Millipore). The ink was sonicated (Ultrawave, 50 Hz) for 1 h, then stirred for 15 h and centrifuged at 20000 rpm for 10 min. The supernatant was discarded and the resulting ink placed in an alumina crucible and pyrolised in a quartz tubular furnace at 900 °C for 2 h, heating rate of 5 °C min^{-1}, under 50 mL min^{-1} N$_2$ atmosphere (BOC gases, O$_2$ free, 99.998% purity). Finally, the sample was cooled under nitrogen before being weighed.

Rotating ring-disk voltammetry was performed using a Metrohm AutoLAB PGSTAT128N potentiostat connected to a rotator (Pine Instruments Inc., USA) in a Faraday cage. The reference electrode was

an Ag/AgCl (sat. KCl) electrode (ALS Inc., E^0 = + 0.197 V vs. SHE) and the counter electrode was a Pt mesh. The RRDE (Pine Instruments Inc., USA) consisted of a GC disk (5.61 mm diameter) and a Pt ring with an area of 0.1866 cm^2, with a collection efficiency of 37%. Prior to each experiment the RRDE was thoroughly polished with consecutive alumina slurries of 1, 0.3 and 0.05 μm (Buehler) and then sonicated to remove any impurities. The catalyst inks were prepared by dispersing different amounts of the as-prepared dual-doped graphene (or pure graphene sourced from PiKem Ltd.), and La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM, PRAXAIR Surf. Tech., surface area: 4.19 m^2 g^{-1}) or manganese (IV) oxide (MnO$_2$, Sigma-Aldrich, 99%), to give a total amount of 5 mg (with the desired composition) in 0.2 mL of isopropyl alcohol (VWR Chemicals), 0.78 mL of ultrapure water and 0.02 mL of 10 wt% Nafion