Supplementary Information

Activation of oxygen evolving perovskites for oxygen reduction by functionalization with Fe-N$_x$/C groups

Rosalba A. Rincón, [a] Justus Masa, [a,*] Sara Mehrpour, [a] Frank Tietz, [b] Wolfgang Schuhmann [a,*]

[a] Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

[b] Forschungszentrum Jülich GmbH, IEK-1, D-52425 Jülich, Germany

1   Experimental

1.1   Synthesis of NC, Fe-N$_x$/C and Fe-N$_x$/C/perovskite

Vulcan® XC72 (Cabot corporation) was dispersed in ultrapure water (50 ml) containing acetic acid (10% v/v). After ultrasonication for 15 min, pyrrole equivalent to a weight ratio of 2:3 (pyrrole:Vulcan® XC72) was added to the suspension. The mixture was further ultrasonicated for 20 min to uniformly disperse the monomer. Afterwards, 5 ml of hydrogen peroxide (30%) was added drop-wise to the suspension under continuous mixing to effect polymerization of the pyrrole. The polypyrrole/Vulcan composite was filtered and dried in air for 24 h, afterwards; the composite was further dried at 80 ℃ in an oven, pulverized and subsequently pyrolyzed at 800 ℃ for 2 h under He gas to obtain nitrogen functionalized carbon powder (NC).

For synthesis of Fe-N$_x$/C, a specific mass of iron phthalocyanine (FePc) was mixed with NC, mass ratio 3:7 (FePc:NC), in a quartz boat, and uniformly dispersed with the aid of acetonitrile and a glass rod, and left to dry under a fume hood before pyrolysis.

Four different OER active perovkites were used for the development of bifunctional composite materials: La$_{0.6}$Sr$_{0.4}$FeO$_3$ (L60SF), La$_{0.76}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (L76SCF), La$_{0.83}$Ca$_{0.15}$Mn$_{0.5}$Co$_{0.4}$O$_3$ (LCaMC) and La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (L58SCF). The Fe-N$_x$/C/perovskite catalysts were prepared by impregnation of the perovskite with FePc and NC on a quartz boat in acetonitrile with the aid of a glass rod for mixing. The mixture was then left to dry under the fume hood, and later pyrolyzed at 700 ℃ for two hours under argon.

1.2 Characterization

Scanning electron microscopy (SEM) images and Energy dispersive X-ray spectroscopy (EDX) were performed using a Quanta 3D FEG scanning electron microscope (FEI™) operated at 20.0 kV and at 30 kV respectively. X-ray diffraction (XRD) measurements were performed using a PANalytical theta-theta powder diffractometer equipped with a Cu-K$_\alpha$ radiation source. To obtain a good signal-to-noise ratio, scans were run from 10 to 80° with a step width of 0.03°. Refinements were done to the XRD spectrum of L58SCF with the software packages "Jana" (Academy of Sciences, Institute of Physics, Prague, Czech Republic) or "GSAS".

1.3 Electrochemical tests

Electrochemical measurements were performed in a conventional three-electrode cell using glassy carbon (Ø 4 mm; HTW, Germany) modified with catalyst films as the working electrode, Ag/AgCl/3 M KCl as the reference electrode and a Pt wire as the counter electrode. The reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE). Prior to the experiments, the glassy carbon electrode was polished on a polishing cloth using alumina pastes of different grain sizes (3.0 - 0.3 μm) to obtain a mirror-like surface, followed by ultrasonic cleaning in water. For the catalyst films, inks were prepared with 5.0 mg of the catalyst per mL of solution. The catalyst powders were dispersed ultrasonically for 30 min in a mixture of water (490 μl), ethanol (490 μl) and Nafion® (5 %, 20 μl). 6 μl of the resulting catalyst suspension was dropped onto the polished glassy carbon electrode to obtain a catalyst loading of ~240 μg cm^{-2}. The electrodes were dried in air at room temperature before the electrochemical tests.

Cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements were carried out in KOH (0.1 M) using an Autolab potentiostat/galvanostat (PGSTAT12, Eco Chemie, Utrecht, The Netherlands) in combination with a speed control unit (CTV101) and a rotating disk electrode rotator (EDI101; Radiometer Analytical, Villeurbanne, France). All experiments for the ORR and the OER were carried out at room temperature at a scan rate of 10 mV s^{-1} after purging the electrolyte with oxygen for 20 min. Before each RDE measurement, a conditioning step was performed by scanning the potential in the non-faradaic window (from 0 to 0.5 vs. Ag/AgCl/3 M KCl), for 10 cycles at 100 mV s^{-1}. Rotating ring-disk electrode (RRDE) measurements were performed on an E7R9 RRDE (Pine Instruments, North Carolina, USA) with a glassy carbon disk and platinum ring of area 0.2475 cm^2 and 0.1866 cm^2 respectively. The percentage of hydrogen peroxide produced was calculated from

the equation $\dfrac{200i_R}{i_D + (i_R/N)}$, where i_D is the disc current and i_R is the corresponding ring current

at a given potential and rotation speed. The collection efficiency (N) of the RRDE electrode was calibrated using in a solution of potassium hexacyanoferrate (5 mM) in KOH (0.1 M).

Long term stability measurements were evaluated using double pulse chronopotentiometry and chronoamperometry in KOH (0.1 M) exposed to the atmosphere and switching between oxygen evolution and oxygen reduction, each pulse lasting one hour and alternating between oxygen evolution at a current density of 1 mA cm^{-2} and oxygen reduction at 0.5 V vs. RHE.

Inhibition studies were performed in KSCN (5 mM) with KOH (0.1 M) as supporting electrolyte. The current was first measured in Argon saturated environment to perform background correction, and after one hour of immersion in KSCN, the current was recorded in O$_2$-saturated environment with a rotation speed of 2500 rpm.

2. Results

2.1 Selectivity of oxygen reduction

To determine the selectivity of oxygen by the new catalyst, rotating disk electrode (RDE) voltammograms obtained at different rotation speeds (Fig. 1) were evaluated using the

Koutecky-Levich equation $\dfrac{1}{i} = \dfrac{1}{i_k} + \dfrac{1}{B\sqrt{\omega}}$, where B = $0.62nFAD^{2/3}v^{-1/6}C^*$ (Levich constant),

and i and i_k are the measured and kinetic current respectively, n is the number of electrons transferred, D is the diffusion coefficient of the analyte, in this case O$_2$ (1.9 x 10^{-5} cm^2 s^{-1}), F is the Faraday constant (96485 C mole^{-1}), A is the geometric area of the electrode (0.2475 cm^2 for RRDE, and 0.1256 cm^2 for the RDE), v is the kinematic viscosity of the electrolyte (0.01 cm^{2}s^{-1}), and C^* is the solubility of oxygen in the electrolyte, which for the case of KOH (0.1 M) was taken to be 1.2 x 10^{-6} mole.
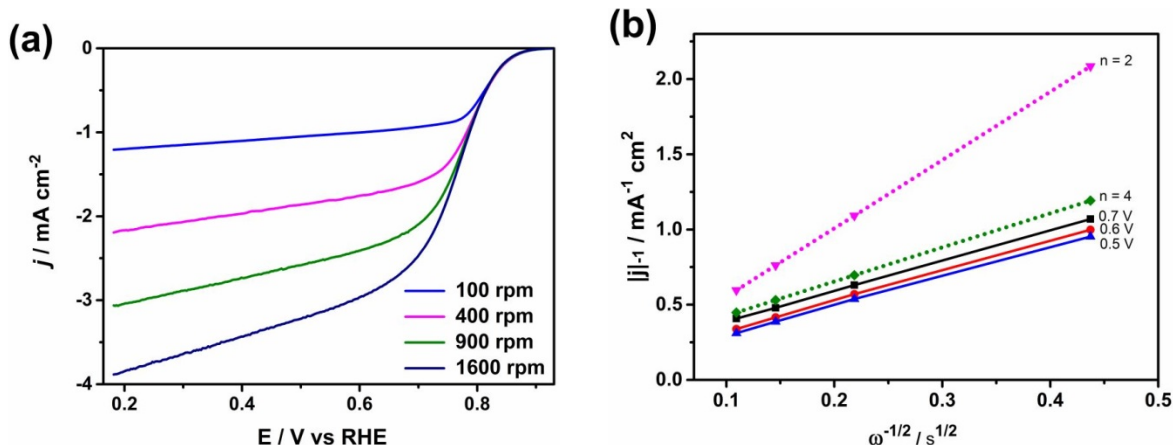
Fig. S1. Linear sweep voltammograms of Fe-N$_x$/C/L58SCF recorded at various electrode rotation speeds in oxygen saturated KOH (0.1 M) at a scan rate of 10 mV s^{-1}, (b) Koutecky-Levich plot, $|j|^{-1}$ (mA^{-1} cm^2) against $\omega^{-1/2}$ (s$^{1/2}$) of the data in (a).

The slopes of the Koutecky-Levich plot, $|j|^{-1}$ (mA^{-1} cm^2) against $\omega^{-1/2}$ (s$^{1/2}$), were; 2.34 at 0.7 V, 2.30 at 0.6 V and 2.28 at 0.5 V, consistent with the theoretical value of 2.27 for a four electron transfer process, as opposed to 4.54 for a two electron transfer process, thus revealing the high selectivity of the catalyst to reduce oxygen mostly to OH$^-$. This was confirmed by rotating-ring disk electrode (RRDE) voltammetry, where the maximum percentage of hydrogen peroxide produced was found to be less than 3.5% at all potentials.
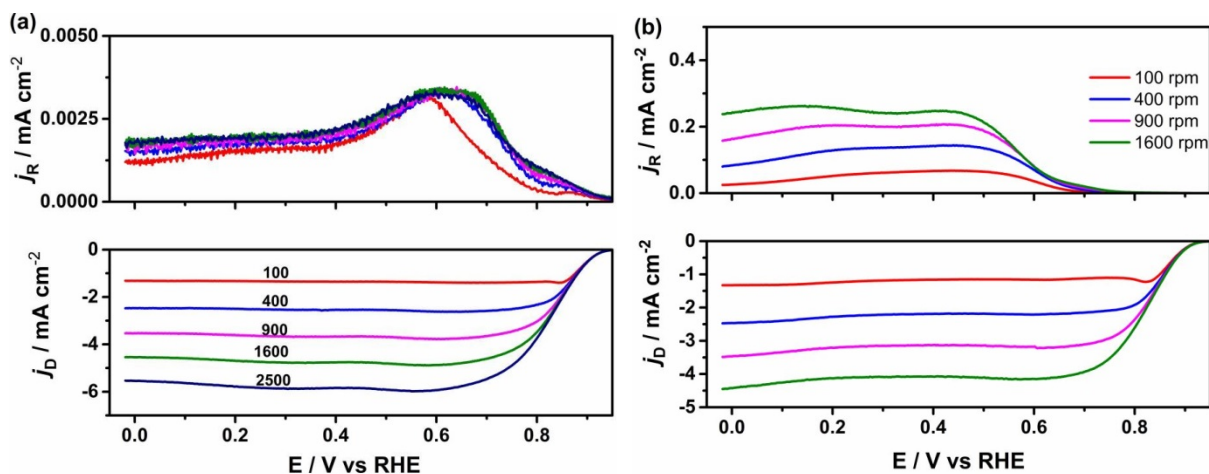
Fig. S2. RRDE voltammograms of (a) Fe-N$_x$/C and (b), recorded at various rotation speeds in oxygen saturated KOH (0.1M) at a scan rate of 10 mVs^{-1}.

2.2   Stability of the Fe-N$_x$/C/L58SCF during ORR and OER

Relatively stable performance of the catalyst was observed with respect to the oxygen reduction reaction (ORR) over a test period of 80,000 seconds (Fig. S3a), whereas for the oxygen evolution reaction (OER), the overpotential gradually increased with time (Fig. S3b).
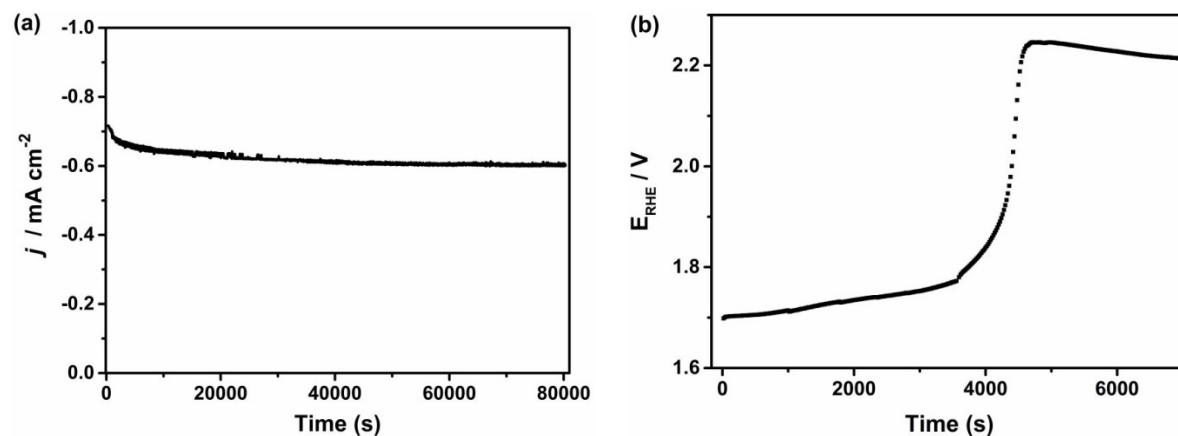

Fig. S3. (a) Chronoamperometric stability measurements for ORR recorded at 0.5 V vs. RHE and rotation at 900 rpm in KOH (0.1 M) exposed to air, (b) chronopotentiometric stability for OER recorded at 1 mA cm^{-2} and electrode rotation at 900 rpm in KOH (0.1 M) exposed to air.

The loss in performance during OER is mainly attributed to accumulation of gas bubbles which partially block the active sites of the electrode. Overtime, the gas bubbles practically cover most of the electrode, even with rotation, leading to a drastic increase of the reaction overpotential. We observed in many cases that the gas bubbles eventually detach the catalyst film from the electrode. It was therefore not possible to assess the real electrochemical stability of the catalyst. Our future research will address strategies for designing the catalyst films to accelerate departure of the gas bubbles and minimize physical detachment of the catalysts in order to enable investigation of their electrochemical stability.

2.3   Effect of SCN$^-$ ions on ORR activity

We have used SCN$^-$ as an ORR inhibitor, in order to demonstrate that Fe represents the ORR active center. The effect of SCN$^-$ ions on the ORR activity of the best performing composite (Fe-N$_x$/C/L58SCF) was probed by submerging the electrode for 1 hour in KSCN (5 mM) and measuring the current response. Fig. S4 shows a comparison of the LSV before and after exposure to SCN$^-$ ions. We observed an overpotential loss of 50 mV at -4 mA/cm^2, and a kinetic current loss of 0.5 mA/cm^2 at 0.5 V$_{RHE}$ (8.6 % loss). This observation indicates that the ORR active site is Fe, since SCN$^-$ can coordinate to Fe$^{(2+/3+)}$ ions, decreasing the availability of active centers for ORR, and therefore the activity of the composite.
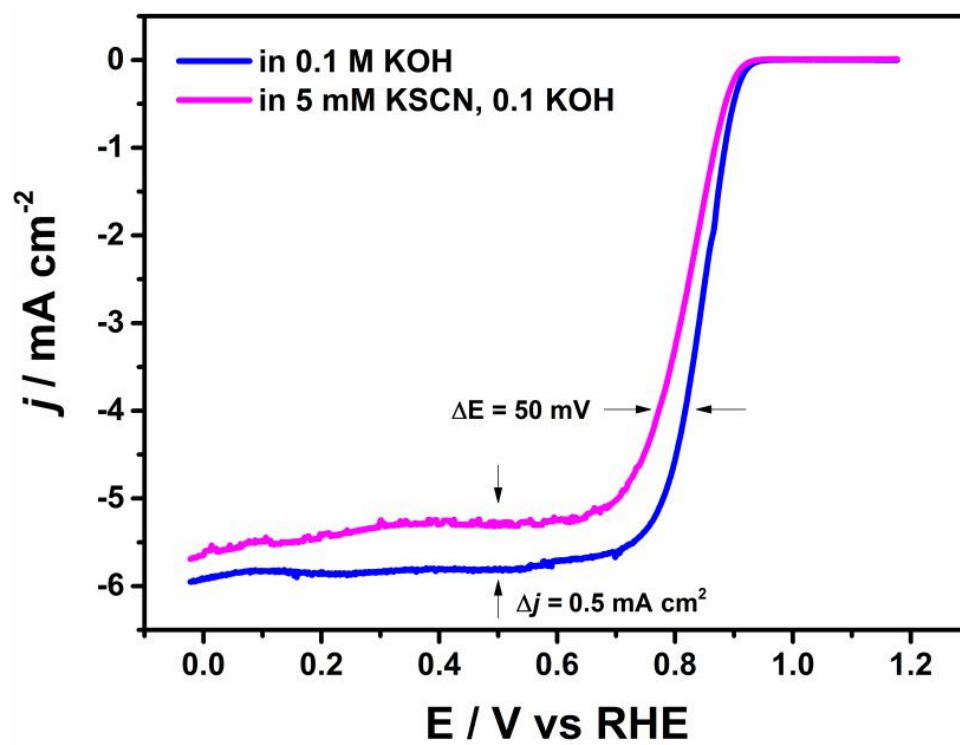
Fig S4. Background-corrected linear sweep voltammogram of Fe-N$_x$/C/L58SCF before and after submersion in KSCN (5 mM, 1 hour), in O$_2$-saturated KOH (0.1 M), 2500 rpm.