Identification of Durable and Non-Durable FeNx Sites in Fe-N-C Materials for Proton Exchange Membrane Fuel Cells

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Jingkun Li[1], Moulay Tahar Sougrati[1], Andrea Zitolo[2], James M. Ablett[2], Ismail Can Oğuz[1],

Tzonka Mineva[1], Ivana Matanovic[3,4], Plamen Atanassov[5], Ying Huang,[5] Iryna Zenyuk,[5]

Andrea Di Cicco,[6] Kavita Kumar,[7] Laetitia Dubau,[7] Frédéric Maillard,[7] Goran Dražić[8] and

Frédéric Jaouen[1]*

1 Institut Charles Gerhardt Montpellier, UMR 5253, CNRS, Université Montpellier, ENSCM,

Place Eugène Bataillon, 34095 Montpellier cedex 5, France

2 Synchrotron SOLEIL, L'orme des Merisiers, BP 48 Saint Aubin, 91192 Gif-sur-Yvette,

France

3 The Department of Chemical and Biological Engineering, Center for Micro-Engineered

Materials (CMEM), University of New Mexico, Albuquerque, NM 87131, USA.

4 Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

5 Department of Chemical and Biomolecular Engineering, National Fuel Cell Research

Center, University of California Irvine, Irvine, 92697, United States

6 School of Science and Technology, Physics Division, University of Camerino, 62032

Camerino (MC), Italy

7 Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP[⊥], LEPMI, 38000

Grenoble, France

[⊥] Institute of Engineering Univ. Grenoble Alpes

8 Department of Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1001

Ljubljana, Slovenia

* To whom correspondence should be addressed.

Email: frederic.jaouen@umontpellier.fr

Abstract

While Fe-N-C materials are a promising alternative to platinum for catalysing the oxygen reduction reaction (ORR) in acidic polymer fuel cells, limited understanding of their *operando* degradation restricts rational approaches towards improved durability. Here we show that Fe-N-C catalysts initially comprising two distinct FeN_x sites (S1 and S2) degrade *via* the transformation of S1 into iron oxides while the structure and number of S2 were unmodified. Structure-activity correlations drawn from end-of-test [57]Fe Mössbauer spectroscopy reveal that both sites initially contribute to the ORR activity but only S2 significantly contributes after 50 h of operation. From *in situ* [57]Fe Mössbauer spectroscopy in inert gas coupled to calculations of the Mössbauer signature of FeN_x moieties in different electronic states, we identify S1 to be a high-spin FeN_4C_{12} moiety and S2 a low- or intermediate-spin FeN_4C_{10} moiety. These insights lay the ground for rational approaches towards Fe-N-C cathodes with improved durability in acidic fuel cells.

69   Catalysis of the ORR is a cornerstone of industrially-relevant electrochemical

70   devices[1] that convert chemical energy into electric power (metal-air batteries,[2,3] fuel cells

71   (FCs),[2,4,5]) or electric power into high-added value products (H_2O_2,[6-8] Cl_2 with oxygen-

72   depolarized cathodes[9-11]). The pH in those devices establishes the ground for selecting

73   materials with promising ORR activity and durability. While proton exchange membrane FCs

74   (PEMFCs) are appealing,[12] their acidic environment is challenging. Platinum-based catalysts

75   now reach high activity and durability,[13,14] but catalysts free of Pt-group-metals remain

76   topical for cost and sustainability reasons. Although metal-nitrogen-carbon (M-N-C) catalysts

77   (M=Fe, Co) have demonstrated high ORR activity,[15-18] their durability in PEMFC is poor.

78   Their most active sites are atomically-dispersed MN_x moieties,[15,16,18] and main degradation

79   mechanisms in acidic medium are demetallation,[19-23] surface carbon oxidation *via* Fenton

80   reactions,[24,25] bulk carbon corrosion,[21,26,27] and protonation of nitrogen groups followed by

81   anion adsorption — a phenomenon particularly important for Fe-N-C catalysts comprising

82   highly basic N-groups.[28] Exacerbated demetallation was recently reported in oxygenated acid

83   medium for highly-active NH_3-pyrolyzed Fe-N-C catalysts, explaining their poor durability

84   in PEMFC.[22,29] The demetallation rate was measured online in acidic aqueous condition,[29] or

85   indirectly assessed by [57]Fe Mössbauer spectroscopy.[22] In contrast, high stability in acidic

86   medium was reported by us for two catalysts exclusively comprising FeN_x moieties, with

87   only 25 % activity decrease after 30,000 load-cycles in Ar-saturated 0.1 M H_2SO_4 at 80°C.[21]

88   However, after 10,000 load-cycles in the same conditions but in O_2-saturated electrolyte, the

89   decrease in activity and number of FeN_x moieties was 65 and 83 %, respectively, forming

90   iron oxide particles during cycling.[30] Carbon corrosion was observed from Raman

91   spectroscopy after load cycles in O_2-saturated electrolyte,[30] while restricted changes in cyclic

92   voltammetry (restricted carbon corrosion) was observed by Dodelet *et al.* for an NH_3-

93   pyrolyzed Fe-N-C after a voltage hold of 6 h at 0.6 V in H_2/air PEMFC at 80°C.[22]

94   Therefore, Fe-N-C catalysts comprising more of the durable FeN_x sites and less of the non-

95   durable ones should be targeted. Before the community can engage in this challenge, the

96   identification of which FeN_x sites are durable and which are not is required. It was revealed

97   with *ex situ* [57]Fe Mössbauer spectroscopy that Fe-N-C catalysts comprise two types of FeN_x

98   sites, labelled D1 (doublet with quadrupole splitting (QS) values of 0.9-1.2 mm·s^{-1}) and D2

99   (QS=1.8-2.8 mm·s^{-1}), both having a similar isomer shift (IS).[15,31,32] By bridging density

100 functional theory calculations on QS-values with *ex situ* Mössbauer spectroscopy, we

101 identified D1 to be a high-spin Fe(III)N_x site (iron site S1) and D2 a low/medium-spin

102 Fe(II)N_x site (iron site S2),[33] in general agreement with two recent studies.[34,35] While these

103 sites are ubiquitous in Fe-N-C catalysts, their respective activity and durability are unknown.

104

105   Here, we separately interrogate S1 and S2 with *in situ, operando* and end-of-test (EoT)

106 spectroscopies (see self-consistent definitions in Supplementary Note 1). With *in situ* [57]Fe

107 Mössbauer spectroscopy in O_2-free PEMFC, we demonstrate that a fraction of S1 is stable,

108 reversibly changing from high-spin ferric to high-spin ferrous state between 0.8 and 0.2 V,

109 while the electronic state of S2 is potential-independent, being ferrous low- or medium-spin.

110 *Ex situ* [57]Fe Mössbauer spectroscopy at 5 K after PEMFC potentiostatic operation reveals that

111 S2 is durable while S1 is not, with corresponding Fe cations forming ferric oxide

112 nanoparticles. We also provide evidence that S2 is the main contributor to ORR activity in

113 PEMFC after short operation time.

114

115

116 **Results**

117 ***Ex situ* characterization of pristine Fe-N-C catalysts**

118   This study was conducted on two Fe-N-C catalysts, previously demonstrated to be

119   free of iron clusters and containing only single-metal-atom FeN_x sites, synthesized as

120   previously reported (see Methods)[15] and labelled $Fe_{0.5}$ (pyrolysis in argon) and $Fe_{0.5}$-950(10)

121   (pyrolysis of $Fe_{0.5}$ in NH_3 at 950 °C for 10 min). Their *ex situ* structure and morphology are

122   reported in Extended Data **Figure 1** and Supplementary **Table 1**, the main *ex situ* differences

123   between them being the higher surface basicity and microporous area of $Fe_{0.5}$-950(10). No Fe

124   particles were observed by transmission electron microscopy (TEM) in both pristine powder

125   catalysts, and the atomic-dispersion of Fe in $Fe_{0.5}$ was further confirmed by STEM (Extended

126   Data **Figure 1g-i**). Their initial ORR activities in PEMFC (**Figure 1a)** are similar to values

127   reported in Ref.15 and representative for state-of-art Fe-N-C catalysts.[18,22,36] NH_3 pyrolysis

128   introduces highly-basic nitrogen groups, increasing the turnover frequency (TOF) of FeN_x

129   sites but leading to decreased durability in PEMFC.[15,17] This was recently explained by

130   higher demetallation rates for NH_3- *vs*. Ar-treated Fe-N-C catalysts in acid medium,[17,29] while

131   demetallation rates were equally low in alkaline medium.[29] These results support the

132   involvement of highly basic nitrogen-groups in a significant fraction of FeN_x sites in $Fe_{0.5}$-

133   950(10), leading to higher TOF but also fast protonation of N-groups in acid medium, leading

134   to demetallation of the most active sites. Due to its high stability in acid,[21] $Fe_{0.5}$ was selected

135   for *in situ* ^{57}Fe Mössbauer spectroscopy in PEMFC. The *ex situ* Mössbauer spectra at 300 K

136   of $Fe_{0.5}$ (powder) and $Fe_{0.5}$-cathode are identical, identifying only D1 and D2 (Extended Data

137   **Figure 2a-b**). However, one cannot exclude the formation of superparamagnetic ferric oxide

138   nanoparticles during cathode preparation, which would contribute with a doublet overlapping

139   with D1 signal from S1 sites.[37] To unveil this degeneracy, the spectra were acquired at lower

140   temperature (5 K), which increases the magnetization time constant of nano ferric-oxides,

141   contributing then with a sextet component,[38,39] while the signal of S1 remains a doublet.[40] At

142   5 K, no sextet was visible for $Fe_{0.5}$ while a broad sextet representing only 9 % of the

143   absorption area, assigned to superparamagnetic ferric oxide, appeared for $Fe_{0.5}$-cathode

144   (Extended Data **Figure 2c-d**). Thus, the low-QS doublet (labelled D1) in the $Fe_{0.5}$-cathode

145   spectrum at 300 K can mainly be assigned to S1 sites.

146

147   *Operando* **X-ray absorption spectroscopy of $Fe_{0.5}$** *in* **PEMFC**

148   *Operando* (extended) X-ray absorption near-edge and fine structure (XANES and

149   EXAFS, respectively) was acquired at Fe K-edge with fast acquisition mode in PEMFC (Cell

150   2,[41] Supplementary **Figure 1a**, Supplementary Note 2). Reversible changes with

151   electrochemical potential were revealed (**Figure 1b**, Extended Data **Figure 3**), confirming in

152   PEMFC the *in situ* and/or *operando* XANES-EXAFS results previously measured in aqueous

153   acidic electrolyte for $Fe_{0.5}$ and other catalysts comprising only/mostly FeN_x sites.[2,16,42,43]

154   *Operando* XANES spectra indicate a Fe(III)/Fe(II) redox transition and conformational

155   changes of a significant fraction of FeN_x sites in the region 0.2-0.8 V (Extended Data **Figure**

156   **3a**), while *operando* EXAFS spectra indicate a change from an average O-Fe(III)N_4 to

157   Fe(II)N_4 coordination as the potential is decreased (Extended Data **Figure 3b**).[42-44] The redox

158   transition is also seen by cyclic voltammetry in acid electrolyte and in line with the decreased

159   average oxidation state of Fe identified by the threshold energy of the XANES spectrum

160   (Extended Data **Figure 3c**).

161

162   *In situ* **Mössbauer spectroscopy of $Fe_{0.5}$ in PEMFC**

163   X-ray absorption spectroscopies (XAS) however fail to provide separate information

164   on S1 and S2. To this end, we resorted to *in situ* [57]Fe Mössbauer spectroscopy with an in-

165   house single-cell PEMFC (Cell 3, Supplementary **Figure 1b**, Supplementary Note 2), whose

166   proper electrochemical response was verified (Supplementary **Figure 2**). The transmitted γ-

167   ray signal was continuously acquired for 36 h during each *in situ* potentiostatic experiments

168   at room temperature, with humidified H_2/argon at anode/cathode. Following the

169   potentiostatic controls shown in Extended Data **Figure 4**, we identified irreversible changes

170   in the Mössbauer spectra of $Fe_{0.5}$-cathode (during the first two cycles, discussed later) and,

171   thereafter, reversible changes triggered by the potential. **Figure 1c-d** shows reversible

172   changes for *in situ* Mössbauer spectra measured at 0.8 and 0.2 V during cycle 4, labelled 0.8

173   V (4) and 0.2 V (4). The hyperfine parameters IS and QS of D1 (labelled D1H for *in situ*

174   spectra, see later) and of D2 are similar at 0.8 V (4) to those measured *ex situ* for the pristine

175    $Fe_{0.5}$-cathode (Supplementary **Table 2**). In contrast, at 0.2 V (4), both the IS and QS values

176   for D1 (labelled D1L, see later) significantly increased, while those for D2 were unmodified

177   (**Figure 1d**, Supplementary **Table 2**, row "0.2 V (4)"). After all potential holds (Extended

178   Data **Figure 4**), we verified with *ex situ* Mössbauer spectroscopy at 5 K that the low-QS

179   doublet (labelled D1H and observed *in situ* at high potential in cycles 1-4) can still be

180   assigned to S1 sites (Supplementary **Figure 3**). D1H and D1L therefore represent the *in situ*

181   Mössbauer signal of S1 sites at high and low potential, respectively. **Figure 1c-d** also

182   identifies a third doublet D3, independent of potential and related to irreversible changes

183   occurring to the $Fe_{0.5}$-cathode during cycle 1 (discussed later).

184

185   We now discuss trends for all *in situ* Mössbauer spectra acquired at various potentials.

186   The spectrum 0.8 V (1) shows the doublets D1-D2 (Supplementary **Figure 4a**), with same IS

187   and QS values as those of the pristine $Fe_{0.5}$-cathode at 300 K (Extended Data **Figure 2b**).

188   However, the ratio D1/D2 is lower in 0.8 V (1) (Supplementary **Table 2**), indicating that

189   some unstable S1 sites were lost during the 36 h-long 0.8 V (1) experiment. From 0.8 V (1) to

190   0.2 V (1), the spectral parameters and intensity of D2 remained unchanged (Supplementary

191   **Figure 4a-b**). This applies also to all subsequent potential holds (Supplementary **Figures 5-**

192   **8**). In contrast, the signal from S1 at high potential (D1H) in 0.8 V (1) resulted in a much less

193 intense central doublet in 0.2 V (1) (grey doublet in Supplementary **Figure 4b**). This

194 indicates demetallation of a significant fraction of sites S1 during the first hold at 0.2 V, in

195 line with 15-40% activity loss after 10k load-cycles in inert gas reported by us for two Fe-N-

196 C catalysts (almost) exclusively comprising FeN_x sites.[21] Since the 0.2 V (1) spectrum was

197 acquired for 36 h, it may be regarded as a time-averaged spectrum reflecting irreversible

198 phenomena. A detailed analysis of the time-dependence of 0.2 V (1) spectrum clearly reveals

199 this (Supplementary **Figure 9**, Supplementary Note 3). During cycles 2-4 however, the

200 switch between D1H and D1L was triggered solely by the electrochemical potential, with

201 distinct IS and QS values (**Figure 2a-b**, Supplementary **Figure 5b**). Regarding doublet D3

202 (IS~1.15·mm s^{-1} and QS~2.5 mm·s^{-1}), it appeared first in 0.2 V (1) (Supplementary **Figure**

203 **4b**) and is unambiguously assigned to high-spin Fe^{2+} species due to its high IS.[45,46] The

204 spectral parameters and intensity of D3 remained almost unchanged from 0.2 V (1) and

205 during all subsequent potential holds (**Figure 2e-f**, Supplementary **Figures 5-8**). From 0.8 V

206 (2) and afterwards, all spectral changes only reflect the reversible potential dependence of the

207 Mössbauer signature from S1 sites (**Figure 2**, Supplementary **Figures 5-7**). To gain

208 understanding on D3, we performed EoT Mössbauer spectroscopy of the $Fe_{0.5}$-cathode at

209 various temperatures, after completing all *in situ* measurements (Supplementary **Figures 3b**,

210 **10-11,** Supplementary **Table 3**, Supplementary Note 4). In summary, the *in situ* D3

211 component is assigned to high-spin Fe^{2+} cations (possibly complexed with Nafion® sulfonic

212 acid groups), formed from the demetallation of a fraction of S1 sites during 0.2 V (1)

213 (scheme in Extended Data **Figure 5**). When exposed to air, such cations form

214 superparamagnetic ferric oxide nanoparticles, overlapping then with D1 at 300 K

215 (Supplementary **Figure 10a-b**). At T ≤ 80 K, they however then contribute with a sextet

216 component with IS and hyperfine magnetic field corresponding to ferric oxide

217 (Supplementary **Figure 10b-f**). A summary of the inter-relation between the Mössbauer

218 components *ex situ, in situ*, and EoT after *in situ* measurements is given in Supplementary

219 **Table 4**.

220

221 **Reversibly-changing *in situ* coordination of S1 with potential**

222 We now discuss the structures and electronic states of S1 and S2. The *in situ* (absence

223 of O_2) Mössbauer signal of the fraction of S1 sites that survived 0.2 V (1) reversibly switches

224 between D1L at 0.2 V and D1H at 0.8 V (**Figure 2a-b**). D1H is identical to D1 measured *ex*

225 *situ* on pristine $Fe_{0.5}$, that we recently identified to be mainly $Fe(III)N_4C_{12}$ periodic or cluster

226 structures in high-spin state, with axial oxygen adsorbates.[33,42] Due to its high IS-value, the

227 assignment of D1L to a high-spin Fe(II) species is straightforward.[45,46] Consequently, only a

228 restricted change in the average iron-spin is expected for $Fe_{0.5}$-cathode between high and low

229 potential. We used a three-electrode cell (Cell 4,[16] Supplementary **Figure 1c**, Supplementary

230 Note 2) to verify this with *in situ* Fe K_β X-ray emission spectroscopy (XES), a technique

231 well-suited to investigate the spin-state of metal centers.[47] The overlapping *in situ* XES

232 spectra at 0.2 and 0.8 V support that the sites S1 are in high-spin at all potentials

233 (Supplementary **Figure 12**). The switch from D1H to D1L signal for S1 is thus the outcome

234 of the reduction from $Fe(III)N_4C_{12}$ to $Fe(II)N_4C_{12}$, also triggering the removal of an axial

235 OH-adsorbate. To further support this, we applied our recently reported DFT methods[33] to

236 calculate the QS-value of different high-spin $OH\text{-}Fe(III)N_4C_{12}$, $OH\text{-}Fe(III)N_4C_{10}$, $Fe(II)N_4C_{12}$

237 and $Fe(II)N_4C_{10}$ models (Supplementary **Figure 13**, the atomic coordinates of the optimised

238 models are provided in Supplementary **Data 1**). While high-spin $OH\text{-}Fe(III)N_4C_{12}$ and OH-

239 $Fe(III)N_4C_{10}$ structures lead to QS-values of 0.6-1.0 $mm \cdot s^{-1}$, matching those of D1H, only the

240 high-spin $Fe(II)N_4C_{12}$ structures lead to QS-values of 1.7-2.0 $mm \cdot s^{-1}$, matching those of D1L

241 (Supplementary **Table 5**). The QS-values of high-spin $Fe(II)N_4C_{10}$ structures are >3.0 $mm \cdot s^{-1}$,

242 significantly higher than those of D1L (Supplementary **Table 5**). These results confirm our

14

243 recent assignment of D1 to high-spin Fe(III)N_4C_{12} structures with axial oxygen ligand,[33] and

244 reveal their switch to high-spin Fe(II)N_4C_{12} structures, without axial ligand, at low potential

245 (D1L). *Operando* EXAFS spectra (Extended Data **Figure 3b**) also support that the Fe(III)-to-

246 Fe(II) reduction is accompanied by desorption of oxygen adsorbates.[42,48] This redox switch is

247 in line with *in situ/operando* XAS on numerous Fe-N-C catalysts [2,16,42,43] and with the

248 significant presence of S1 in Fe-N-C catalysts.[15,31,32,42] Here, we show that S1 undergoes this

249 redox transition, but not S2. We then analysed the potential-dependence of the S1 hyperfine

250 parameters. **Figure 3a-b** shows that they can be divided into those below 0.5 V and those

251 above (D1L and D1H, respectively). For comparison, **Figure 3c** reports the DFT-calculated

252 QS for high-spin OH-Fe(III)-N_4C_{12} and high-spin Fe(II)-N_4C_{12} structures, demonstrating that

253 our DFT method correctly reproduces the change in QS. Supplementary **Table 4** summarises

254 the main findings on D1H and D1L and how they inter-relate with the site S1.

255

256 **Different fates of sites S1 and S2 in an operating PEMFC**

257 We then attempted to investigate the electronic states and durability of S1 and S2 with

258 *operando* (O_2) Mössbauer spectroscopy. However, this proved impossible for S1. After a

259 single potential hold at 0.2 V in O_2, no S1 sites were observed in the EoT Mössbauer

260 spectrum at 5 K while two sextets appeared, assigned to ferric oxide particles (Extended Data

261 **Figure 6c**). The relative amount of sextets is much higher than in the pristine $Fe_{0.5}$-cathode

262 (Extended Data **Figure 6a**), supporting that the major fraction of S1 sites survived the MEA

263 preparation, but transformed to ferric oxides during fuel cell testing. The cathode was also

264 characterized before and after the potential hold with TEM (Extended Data **Figure 6b,d**) and

265 XRD (Extended Data **Figure 6e**). Only TEM after operation identified Fe particles of *ca* 5-15

266 nm size. The *operando* Mössbauer spectra were comparable at OCP and 0.2 V (not shown)

267 which, combined with the EoT spectrum at 5 K, suggests that the D1-like signal identified at

268   0.2 V under *operando* conditions already originated from ferric oxides instead of S1 sites.

269   The presence of ferric oxides at 0.2 V in turn suggests those particles are not electronically

270   connected to the cathode, but only in contact with Nafion phase. In contrast, the parameters

271   and absolute intensity of D2 were unmodified before and after 0.2 V hold in O_2

272   (Supplementary **Table 6**). This indicates that the electronic state of S2 is potential-

273   independent in the range 0.2-0.9 V and independent of the presence/absence of O_2. This in

274   turn indicates that S2 is either not accessible to O_2 or binds O_2 weakly, in line with our *ex situ*

275   analysis.[33] The activity of $Fe_{0.5}$-cathode before and after *operando* measurements (Cell 3) was

276   measured in Cell 1 at 80°C. A restricted ORR-activity decrease from 23 to 15 mA·cm^{-2} is

277   observed at 0.8 V (Extended Data **Figure 6f**). The remaining activity is much higher than that

278   of the Fe-free N-doped carbon matrix (N-C),[15] implying that either S2 or ferric oxides are

279   active. To evaluate the ORR activity of the latter, we precipitated Fe_2O_3 nanoparticles on the

280   same N-C support. The activity of Fe_2O_3/N-C above 0.7 V is within reproducibility equal to

281   that of N-C, implying no or negligible ORR activity of Fe_2O_3 (Supplementary **Figure 14**).

282

283   To follow spectral changes as a function of operating time, a series of cathodes was

284   prepared from a same $Fe_{0.5}$ batch and operated at 0.5 V in Cell 1 for either 5, 10, 25 or 50 h.

285   Polarisation curves were recorded before and after each experiment. Each MEA was

286   characterized with EoT ^{57}Fe Mössbauer spectroscopy at 5 K (**Figure 4a-c**, Supplementary

287   **Figure 15**, Supplementary **Table 7**). The fittings indicate unmodified spectral parameters and

288   absolute intensity for D2 with operation time, continuously decreasing signal intensity for D1

289   and continuously increasing signal intensity for the two sextets, assigned to

290   superparamagnetic ferric oxide (**Figure 4a-c**, Supplementary **Figure 15**). EoT XANES

291   reveals only minor changes (Supplementary **Figure 16a)** while EXAFS spectra after 10-50 h

292   reveal a small increase in the Fe-Fe signal at ~2.7 Å, matching the Fe-Fe distance in Fe_2O_3

293   (Supplementary **Figure 16b**). X-ray computed tomography performed *ex situ* after 50 h of

294   operation at 0.5 V shows the presence of Fe particles (**Figure 4e**, Supplementary **Figure 17a**).

295   Most particles are present on or near the outer surface of the N-C matrix. Size distribution

296   analysis (Supplementary **Figure 17b**) reveals the presence of particles 5 to 60 nm in size,

297   with the most frequent sizes being between 5 and 10 nm (47.5%). The initial and final

298   polarisation curves indicate a sharp activity decrease after 5 h operation at 0.5 V followed by

299   a slow but steady activity decrease (**Figure 4d**, Supplementary **Figure 18a**).

300

301   **Evidence for ORR activity contributions from S1 and S2 sites**

302   To identify structure-activity relationships, we plotted the absolute area of each

303   spectral component and the current density at 0.8 V as a function of time (**Figure 5a-d**). The

304   results indicate a trend of decreased activity with operation time, decreasing amount of sites

305   S1, increasing amount of ferric oxides (sextets) and unchanged amount of sites S2. Based on

306   this, we plotted in **Figure 5e** the current density at 0.8 V as a function of the absolute

307   absorption area for either D1 or (D1+D2). Except for the initial activity measurements, the

308   results reveal a linear correlation between the activity and either D1 or (D1+D2),

309   demonstrating that S1 contributes to ORR activity. The data for the initial activity (star

310   symbol) is an outlier and this can be explained by a higher TOF of Fe-based sites during the

311   first polarisation curve. This hypothesis is in line with our recent work that demonstrated

312   decreased TOF of Fe-based sites by chemical reaction of $Fe_{0.5}$ with H_2O_2.[25] The activity drop

313   from 0 to 5 h of operation is thus assigned to both decreased TOF *via* mild surface oxidation

314   of carbon (vertical arrows in **Figure 5e**), and decreased number of S1 sites (arrows along the

315   dashed lines in **Figure 5e**). After 5 h operation, the TOF of the Fe sites seems stabilized,

316   leading to linear correlations between the overall activity and either D1 or D1+D2. The

317   extrapolation at x = 0 of the plot of activity *vs.* absolute area of D1 leads however to a

318 positive y-intercept, indicating that the $Fe_{0.5}$-cathode should have a significant ORR activity

319 even in the absence of S1. This is supported by the results after operation at 0.2 V in O_2

320 (Extended Data **Figure 6**). In contrast, the extrapolation at x = 0 of the plot of activity *vs.*

321 absolute area of D1H+D2 is near zero, supporting the fact that both S1 and S2 are ORR-

322 active in acidic medium. A rigorous analysis shows that this near-zero y-intercept can be

323 interpreted either as S2 sites being all located on the surface and having a similar TOF as S1,

324 or only a fraction of S2 sites are on the surface and implying then a higher TOF than S1

325 (Supplementary Note 5). From EoT Raman spectroscopy, no carbon corrosion was identified

326 (Supplementary **Figure 18b**). We verified that these trends also apply to the initially more

327 active $Fe_{0.5}$-950(10) catalyst (Extended Data **Figure 7,** Supplementary **Table 8**, and

328 Supplementary **Note 6**). The relative % area of D1 decreased from 32 to 6 % during 50 h at

329 0.5 V for $Fe_{0.5}$-950(10) and from 43 to 6% for $Fe_{0.5}$. For D2, the relative % area decreased

330 from 40 to 38 % in 50 h for $Fe_{0.5}$-950(10) but slightly increased from 49 to 51 % for $Fe_{0.5}$.

331 The variation of $\pm$ 2 % in D2 is within the error, and D2 can be considered durable in both

332 cathodes. Comparative STEM-EDX analysis of $Fe_{0.5}$-950(10) fresh and aged (50 h at 0.5 V)

333 cathodes identify few large Fe particles in the fresh cathode but numerous Fe nanoparticles

334 after aging (Supplementary **Figure 19**). In addition, the correlation between Fe and F

335 mapping in the aged cathode suggests that Fe clustering is linked to the presence of Nafion

336 ionomer (Supplementary **Figure 20**).

337

338 **Conclusions**

339 　　In conclusion, we identify with Mössbauer spectroscopy the high-spin S1 site and the

340 low- or intermediate-spin S2 site, both assigned to FeN_4 moieties but embedded in different

341 ways in the carbon matrix. Iron in the site S1 switches oxidation state III/II in the region 0-1

342 V while S2 does not, remaining Fe(II). We also identify that both sites initially contribute to

343   the ORR activity of Fe-N-C in acidic medium. However, S1 is not durable in operating

344   PEMFC, quickly transforming to ferric oxides (**Figure 6**). In contrast, S2 is shown to be

345   more durable, with no measurable decrease of the number of active sites after 50 h operation

346   at 0.5 V. The lack of change of oxidation state for Fe in S2 in the region 0-1 V is not

347   contradictory with catalysis. For example, we showed with *in situ* XAS that CoN_x sites do not

348   change oxidation state in acidic medium in the same region but catalyze ORR.[16,44] The

349   degradation of S1 into ferric oxides may be a direct or indirect demetallation, the indirect

350   pathway possibly triggered by localized carbon surface oxidation or protonation of highly

351   basic nitrogens involved in S1. The stability of S2 may be due to a more graphitic local

352   structure, lower amount of reactive oxygen species (ROS) produced during ORR in acid, or

353   its sub-surface location activating the N-doped carbon top-surface. These results and/or

354   methods are of high interest to the improved understanding of Fe-N-C materials for

355   application in PEMFC but also in anion-exchange membrane fuel cells and for CO_2 electro-

356   reduction.[49-50] For PEMFC application, further efforts should be devoted to increasing the site

357   density of S2 sites and/or to stabilize S1 in acidic and oxygenated environment. The former

358   goal might be achieved by depositing a thin overlayer of N-doped carbon on top of Fe-N-C

359   (possibly transforming S1 into S2 sites) and the latter goal by adding co-catalysts (to

360   scavenge H_2O_2 or ROS formed during ORR in acid medium) or by integrating S1 sites in a

361   more graphitic carbon support. In addition, the targeted removal of sites S1 before integrating

362   Fe-N-C materials in PEMFC cathodes would avoid the formation of ferric oxides under

363   *operando* conditions, in turn likely forming ROS in the presence of H_2O_2.

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Figure 1. Initial activity and reversible spectral changes of Fe with PEMFC potential. (**a**) PEMFC Tafel plots of $Fe_{0.5}$ and $Fe_{0.5}$-950(10); (**b**) Fe K-edge XANES spectra measured under *operando* conditions in PEMFC as a function of potential; *in situ* ^{57}Fe Mössbauer spectra at 0.8 V (**c**) and 0.2 V (**d**) acquired during the fourth cycle. For (**a**), the cell temperature was 80 ^{o}C, the flow rates of O_2 and H_2 were 60 sccm with 100% relative humidity, the gauge pressure was 1 bar and the cathode loading was 4 mg·cm^{-2}. For (**b**), all the testing conditions were the same as (**a**), except that no backpressure was applied. For (**c-d**), the cell was at room temperature, the humidifiers were at 50 ^{o}C, Ar and H_2 gases were fed at cathode and anode respectively, and no backpressure was applied. Each Mössbauer spectrum was collected for 36 hours. D1H is the Mössbauer signature of S1 sites at high potential while D1L is their signature at low potential.

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Figure 2. Effect of PEMFC potential on doublets from fitted *in situ* Mössbauer spectra. The spectral doublet D1 (**a**), D2 (**c**) and D3 (**e**) resulting from the fittings, and the corresponding IS and QS values of D1 (**b**), D2 (**d**) and D3 (**f**) at 0.8 V (2), 0.2 V (2), 0.8 V (4) and 0.2 V (4). The number in parentheses represents the cycle number. In (**a**), (**c**) and (**e**), solid curve: 0.8 V (2); dashed curve: 0.2 V (2); ×: 0.8 V (4); ·: 0.2 V (4). In (**b**), (**d**) and (**f**), □: QS; ●: IS. D1H is the Mössbauer signature of S1 sites at high potential while D1L is their signature at low potential. The experimental spectra and all fitted components from which the **Figures 2a, 2c** and **2e** were made can be seen in Supplementary **Figure 6**.

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Figure 3. Experimental and calculated values of hyperfine parameters *vs*. potential.
Reversible change of IS- (**a**) and QS-values (**b**) of the spectral component D1 *vs*.
electrochemical potential. The error bars in (a) and (b) at 0.8 and 0.2 V represent the standard
deviation from three separate measurements on different cycles. (**c**) The QS-values calculated
with PBE/DZVP2 method for different FeN_4C_{12} model structures in high-spin, with/without
oxygen adsorbate. The structures 1e, 1f and 2e are given in Supplementary **Figure 13**. QS-
values calculated for FeN_4C_{10} model structures are given in Supplementary **Table 5**.

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Figure 4. Characterisation of Fe$_{0.5}$-cathode after operation at 0.5 V in PEMFC. (**a**) *Ex
situ* ^{57}Fe Mössbauer spectrum at 5 K of the pristine Fe$_{0.5}$-cathode. EoT Mössbauer spectra at
5 K of the Fe$_{0.5}$-cathode after a hold at 0.5 V for 5 h (**b**) and 50 h (**c**). (**d**) The corresponding
Tafel plots. The inset in (a), (b) and (c) shows the Tafel plot trace, the thicker curve
corresponding to each spectrum. The cell temperature was 80 ^{o}C, 60 sccm O_2 and H_2 gases
with 100% relative humidity were fed at cathode and anode respectively, the gauge pressure
was 1 bar, and the cathode loading was 4 mg·cm^{-2}. (**e**) Volume-rendered FeO_x particles (left)
and FeO_x particles superimposed onto the morphology of support material (right) of the Fe$_{0.5}$-
cathode after a hold at 0.5 V for 50 h, obtained from X-ray computed tomography with phase
contrast for soft elements (mainly C and N) and absorption contrast for hard elements (*i.e.*
Fe).

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413   **Figure 5**. **Correlations between FeN$_x$ site amount in Fe$_{0.5}$-cathode and activity over time.**

414   (**a**) Current density of the Fe$_{0.5}$-cathode at 0.8 V *vs.* duration of operation at 0.5 V in H$_2$/O$_2$

415   PEMFC, absolute absorption areas of D1 (**b**), D2 (**c**) and sextets (**d**) *vs.* duration of operation

416   at 0.5 V in H$_2$/O$_2$ PEMFC. (**e**) The current density of Fe$_{0.5}$-cathodes at 0.8 V as a function of

417   the absolute absorption area for D1 and D1+D2. The absolute absorption area of a given

418   spectral component is proportional to the number of corresponding sites in the cathode.

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424   **Figure 6**. **Coordination or structural changes of the sites S1 and S2 under *in situ* or**

425   ***operando* conditions.** The site S1 is a high-spin FeN$_4$C$_{12}$ structure, undergoing reversible

426   change of Fe oxidation state from III to II *in situ* (no O$_2$) for the most stable S1-sites fraction

427   (D1H to D1L double-sided black arrow), while the less stable fraction of S1 sites irreversibly

428   transforms *in situ* into high spin Fe^{2+} (D1H to D3, single-sided black arrow). When exposed

429   to ambient air for EoT measurement following the *in situ* measurement, high spin Fe^{2+}

430   transform into ferric oxides (D3 to Fe$_2$O$_3$, single-side red arrow). S1 sites irreversibly

431   transform into ferric oxides under *operando* conditions when catalysing the ORR (single-

432   sided red arrow), most probably *via* a fast intermediate stage involving the leaching of Fe^{2+}

433   cations (D3) before the oxide growth may start. S2 sites do not change oxidation state and are

434   stable both *in situ* and *operando* (double-sided arrows).

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436 **Methods**

437 **Synthesis.** The synthesis of $Fe_{0.5}$ and $Fe_{0.5}$-950(10) was reported previously.[15] Catalyst

438 precursors were prepared from a Zn(II) zeolitic imidazolate framework (Basolite Z1200 from

439 BASF, labelled ZIF-8), Fe(II) acetate (Fe(II)Ac), and 1,10-phenanthroline (Phen). ^{57}Fe(II)Ac

440 was used as iron precursor for all Mössbauer studies. For *operando* XAS, natural Fe(II)Ac

441 was used. The catalyst $Fe_{0.5}$ was synthesized via the dry ball-milling of ZIF-8 (800 mg), Phen

442 (200 mg) and Fe(II)Ac (16 mg) in a zirconium oxide crucible filled with 100 zirconium oxide

443 balls (5 mm diameter) at 400 rpm for 2 hours (Fritsch Pulverisette 7 Premium, Fritsch, Idar-

444 Oberstein, Germany). The subscript in $Fe_{0.5}$ corresponds to the Fe content (wt %) in the entire

445 catalyst precursor before pyrolysis. Then the mixed precursor was pyrolyzed in flash mode in

446 Ar at 1050 ^{o}C for 1 hour. Owing to a mass loss of 65–70 wt % during pyrolysis in Ar, caused

447 by volatile products formed from ZIF-8 and Phen, the iron content in $Fe_{0.5}$ is about three

448 times the iron content in the catalyst precursor. $Fe_{0.5}$ was subjected to a second flash pyrolysis

449 for 10 min at 950 ^{o}C in NH_3, yielding $Fe_{0.5}$-950(10). The mass loss of carbon during NH_3

450 pyrolysis was 25–31%, further increasing the iron content.

451 To synthesize Fe_2O_3/N-C, the Fe-free N-C was firstly synthesized identically with $Fe_{0.5}$-950

452 except for the first ball-milling step, where no Fe(II)Ac was added. Then 15 mg of

453 $FeCl_2 \cdot 4H_2O$ was dissolved in 7.5 mL H_2O/ethanol solution (v:v=24:1). Then 300 mg N-C

454 was added, and well-mixed *via* sonication for 1 hour. The obtained slurry was stirred

455 continuously for another 48 hours, followed by filtration, washing with water, and dry in the

456 oven at ~50 ^{o}C overnight. The Fe_2O_3/N-C sample was obtained by a final heat treatment at

457 200 ^{o}C for 2 hours in Ar with a ramping rate of 5 ^{o}C·min^{-1}. The Fe content in Fe_2O_3/N-C was

458 found to be 1.3 wt.% by X-ray fluorescence (XRF) spectroscopy.

459 **XRF.** The metal content in Fe_2O_3/N-C was measured *via* X-ray XRF spectroscopy (Axios

460 Max from PANanalytical, Netherlands). Fe_2O_3/N-C powder was mixed with boric acid as a

461   binder in a ratio of 1:3 by weight *via* ball-milling at 400 rpm for 30 min. Then 200 mg of the

462   mixture was pelletized as a disk of 13 mm diameter for XRF measurements. The calibration

463   curve was performed using 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 wt% Fe in a mixture of Fe(II)Ac and

464   Vulcan XC72R. The Vulcan XC72R (mixed with Fe(II)Ac) were mixed with boric acid in a

465   ratio of 1:3 by weight *via* ball-milling at 400 rpm for 30 min, and then 200 mg of the mixture

466   was pelletized as a disk of 13 mm diameter.

467   **XRD.** X-ray diffraction patterns were recorded using a PANanalytical X'Pert Pro powder X-

468   ray diffractometer with Cu Kα radiation.

469   **STEM.** Probe Cs-corrected scanning transmission electron microscope Jeol ARM 200 F,

470   equipped with a cold field emission electron source, was used for imaging atomically-

471   dispersed FeN_xC_y moieties in $Fe_{0.5}$ pristine powder. To minimize the beam damage, 80 keV

472   and low beam current were used. High-angle annular dark-field (HAADF) images were

473   obtained using 68-180 mrad collection half-angles at 24 mrad probe convergence semi-angle.

474   Images were filtered with non-linear filter which is a combination of low-pass and Wiener

475   filters. The presence of iron and nitrogen was confirmed with Gatan Quantum ER dual

476   Electron Energy-loss Spectroscopy system.

477   **TEM and STEM-EDX.** A JEOL 2010 Transmission Electron Microscopy operated at 200

478   kV was used to examine Fe-N-C cathodes before testing or at EoT. The resolution was 0.19

479   nm. Elemental mapping was performed on fresh/aged Fe0.5-950(10) cathode using a 200 kV

480   JEOL 2100F microscope equipped with a retractable large angle Centurio Silicon Drift

481   Detector (SDD) detector. The Fe *K*, C *K* and O *K* lines and the *K*-factors specified by the

482   JEOL software were used for elemental quantification.

483   **Raman spectroscopy**. Raman spectra were collected using a LabRAM ARAMIS Raman

484   microscope with a 473 nm laser.

485 **N$_2$ sorption isotherms acquisition and analysis**. N$_2$ adsorption/desorption was performed at

486 liquid nitrogen temperature (77 K) with a Micromeritics ASAP 2020 instrument. Prior to the

487 measurements, all samples were degassed at 200 °C for 5 h in flowing nitrogen to remove

488 guest molecules or moisture. The pore size distributions were calculated by fitting the full

489 isotherm with the quench solid density functional theory model with slit pore geometry from

490 NovaWin (Quantachrome Instruments).

491 **Basicity measurement of pristine Fe-N-C powders**. The basicity measurement of Fe$_{0.5}$ and

492 Fe$_{0.5}$-950(10) has been reported elsewhere.[15] A solution with pH 6.0 was first prepared by the

493 titration of a 0.1 M H$_2$SO$_4$ solution by 0.1 M KOH. Then 40 mg catalyst was dispersed into

494 20 ml aqueous solution with an initial pH (pH$_i$) of 6.0. The solution was constantly saturated

495 with N$_2$ to avoid acidification from air. The final pH (pH$_f$) after the dispersion of the catalyst

496 was measured once the pH meter indicated a stable value.

497 **Electrochemical characterisation.** The ORR activities of Fe$_{0.5}$ and Fe$_{0.5}$-950 were

498 investigated in a single-cell PEMFC (Cell 1, see also Supplementary Note 2). For the

499 membrane electrode assembly (MEA), cathode inks were prepared by sonicating for 1 hour

500 the mixture of 20 mg of catalyst, 652 μL of a 5 wt% Nafion solution containing 15–20%

501 water, 326 μL of ethanol and 272 μL of de-ionized water. Then, three aliquots of 405 μl of

502 the catalyst ink were successively deposited on the microporous layer of a 4.84 cm^2 gas

503 diffusion layer (Sigracet S10-BC). The cathode was then placed at 60 °C to dry for 2 hours.

504 The anode used for all PEMFC tests in Cell 1 was 0.5 mg$_{Pt}$·cm^{-2} on Sigracet S24-BC. Nafion

505 NRE-211 was used as membrane. No hot-pressing was applied in order to easily peel off the

506 cathode for EoT characterisation. PEMFC tests were performed with a single-cell fuel cell

507 with serpentine flow field (Fuel Cell Technologies) using an in-house test bench and a

508 Biologic potentiostat with a 50 A load and EC-Lab software. The fuel cell temperature was

509 80 °C, the humidifiers were set at 85 °C and the inlet pressures were set to 1 bar gauge for

510   both anode and cathode sides. The flow rate for humidified H_2 and O_2 gases was 60 sccm

511   downstream. No break-in was applied before recording the first polarisation curve.

512   Polarization curves were recorded by scanning the voltage at 1 mV·s^{-1}.

513   ***Ex situ* and *operando* XAS.** Fe K-edge X-ray absorption spectra were collected at room

514   temperature at SAMBA beamline (Synchrotron SOLEIL). The beamline is equipped with a

515   sagittally focusing Si 220 monochromator, and X-ray harmonics are removed by two Pd-

516   coated mirrors. For *ex situ* measurements on pristine Fe-N-C catalysts, the powders were

517   pelletized as disks of 10 mm diameter with 1 mm thickness, using Teflon powder (1 μm

518   particle size) as a binder and XAS measured in transmission mode. For *ex situ* measurements

519   on Fe-N-C cathodes (before testing or at EoT), XAS was acquired in fluorescence mode. For

520   *operando* XAS experiments, MEAs were prepared identically as for measurements in the

521   commercial PEMFC (Cell 1). The design of the PEMFC used for *operando* XAS study (Cell

522   2, see also Supplementary Note 2) was reported in Ref. 41. The cell temperature was 80 $^{\circ}$C,

523   60 sccm O_2 and H_2 with 100% relative humidity were fed at cathode and anode respectively,

524   and the cathode loading was 4 mg·cm^{-2}. No backpressure was applied.

525   *Operando* measurements were performed by recording the Kα X-ray fluorescence of Fe with

526   a Canberra 35-elements monolithic planar Ge pixel array detector.

527   ***Ex situ* and *in situ* Mössbauer spectroscopy.** ^{57}Fe-enriched Fe(II)Ac was used as iron

528   precursor for all Mössbauer studies. The ^{57}Fe Mössbauer spectrometer (Wissel, Germany)

529   was operated in transmission mode with a ^{57}Co: Rh source. The velocity driver was operated

530   in constant acceleration mode with a triangular velocity waveform. The velocity scale was

531   calibrated with the magnetically split sextet of a high-purity α-Fe foil at room temperature.

532   The spectra were fitted to appropriate combinations of Lorentzian profiles representing

533   quadrupole doublets, sextets by least-squares methods. IS values are reported relative to α-Fe

534   at room temperature. Unless otherwise mentioned in the Supplementary **Tables 2, 3, 6-8**, the

535   fittings were performed with unconstrained parameters (relative area, IS, QS, LW, H) for

536   each spectral component. For *ex situ* measurements on pristine Fe-N-C catalysts, powders

537   (20-30 mg) were mounted in a 2 cm^2 holder. For *ex situ* measurements on Fe-N-C cathodes,

538   before testing or at EoT, 5 cm^2 electrodes were cut into four pieces and stacked on each other.

539   Mössbauer measurements below 100 K were performed in a helium flow cryostat (SHI-850

540   Series from Janis, USA). For *in situ* Mössbauer experiments, MEAs were prepared as

541   described for testing in the commercial PEMFC (Cell 1), except that the anode was 0.1 mg$_{Pt}$

542   cm^{-2} to maximize γ-ray transmission through the cell. The design of the PEMFC for *in situ*

543   Mössbauer spectroscopy (Cell 3, see also Supplementary Note 2) is shown in Supplementary

544   **Figure 1b**. The cell was at room temperature, the humidifiers were at 50 ^{o}C, Ar and H$_2$ gases

545   were fed at cathode and anode respectively, and no backpressure was applied. The Mössbauer

546   signal was continuously acquired for 36 hours at each cathode potential.

547   ***In situ* XES.** Fe K$_\beta$ X-ray emission spectra were collected at room temperature using a 1m

548   radius Germanium 620 analyzer crystal at GALAXY inelastic scattering end-station

549   (Synchrotron SOLEIL).[51-52] The incident energy was 8500 eV (using a silicon double-crystal

550   monochromator) and the focused beam size was 30 [ver.] x 90 [hor.] μm^2. The sample,

551   analyser crystal and silicon drift detector were all arranged in a vertical Rowland circle

552   geometry and air absorption was reduced by using helium flight paths. The electrochemical

553   cell (Goodfellow cat. C 000200/2) used for *operando* XES in liquid electrolyte with a three

554   electrode system is the same as the one previously for *in situ* or *operando* XAS

555   measurements (Cell 4, see also Supplementary Note 2).[16] Catalyst inks were prepared by

556   mixing 10 mg catalyst with 50 μL de-ionized water and 100 μL of 5 wt% Nafion® solution

557   with ultrasounds. A 50 μL aliquot was then pipetted on ~3 cm^2 circular area of a 100-μm-

558   thick graphite foil, resulting in a catalyst loading of ~1 mg·cm^{-2}. The graphite foil with

559   deposited catalyst then served as a working electrode, Ag/AgCl and Pt were used as reference

560   and counter electrodes, respectively. The cell was filled with 0.5 M H_2SO_4 and saturated with

561   N_2 by continuously bubbling gas in the electrolyte.

562   **X-ray computed tomography (CT).** X-ray CT imaging was performed at the Advanced

563   Photon Sources (APS) at Argonne National Laboratory (ANL) using Beamline 32-ID, with 8

564   keV energy and 0.4 s exposure time. Fresnel zone plates with grading of 44.6 nm were used

565   to achieve resolution of 44.6 nm. Zernike phase contrast was used to detect soft elements,

566   whereas absorption contrast was used for imaging hard materials. Image phase retrieval and

567   reconstructions were performed using TomoPy.[53] The volume-rendering structure and

568   analysis were done in Dragonfly 4.1.[54] The calculated volume-to-surface area ratio was

569   considered as the sizes of the particles. The surface area was calculated by pixel-wise method.

570   **DFT computation.** Density functional theory (DFT) spin-polarized calculations were carried

571   out with the cluster and periodic approaches using respectively, deMon2k.6.0.2 developers

572   version[55,56] and VASP[57,58] computer programs on graphene sheets (with defects) integrating

573   various moieties from the ferrous and ferric FeN_4C_{10} and FeN_4C_{12} sub-groups. The

574   considered cluster and periodic models are reported in Supplementary **Figure 13**. The

575   dangling bonds in all structures were saturated with hydrogen atoms. In the cluster

576   calculations, the electrons of the C, H and N atoms are described by triple-ξ basis set and of

577   Fe by double-ξ plus polarization (DZVP2).[59] Electronic exchange and correlation effects

578   were described within the generalized gradient approximation (GGA) in the

579   Perdew−Burke−Ernzerhof (PBE) parametrization.[60,61] No symmetry constraints were

580   imposed. In deMon2k code, for all atoms, automatically generated auxiliary functions up to

581   orbital quantum number, $l = 3$ were used for fitting the density with the GGA functionals.[62]

582   The GGA functionals were also coupled to an empirical dispersion (D) term.[63] A quasi-

583   Newton method in internal redundant coordinates with analytical energy gradients was used

584   for structure optimization of ferrous and ferric models in high spin state. For the numerical

585 integrations of the XC energy and potential, we used an adaptive grid with tighten threshold

586 (10^{-8}a.u.).[64] The convergence was based on the Cartesian gradient and displacement vectors

587 with thresholds of 10^{-3}a.u. and the energy convergence was set to 10^{-7}a.u. The DFT

588 calculations with periodic boundary conditions, carried out with VASP code, used the models

589 2e and 2a to build the unit cells for periodic calculations. In the case of the cluster model 1e,

590 the corresponding periodic structure 2e was modelled using a cell size 17.19 Å×20.89 Å. In

591 the case of model 1a, the corresponding periodic structure 2a was constructed using cell size

592 of 9.94 Å×12.64 Å. Vacuum region of 15 Å was introduced in the *z*-direction in order to

593 eliminate interactions between the graphene sheet and its periodic images. All the DFT

594 calculations with periodic boundary conditions (PBC) were performed using PBE exchange-

595 correlation functional and VASP 5.2 recommended projector augmented-wave

596 pseudopotentials.[65,66] For the calculation of structural and electronic properties, standard

597 PAW potentials supplied with VASP were used, with 4 valence electrons for C (2s2 2p2),

598 with 5 electrons for O (2s 2p3), 8 valence electrons for Fe (4s2 3d6), and 6 valence electrons

599 for O (2s 2p 4), respectively. Electric field gradients at the positions of the Fe nuclei were

600 calculated using the method reported in reference[67] as implemented in VASP. When

601 calculating electric field gradient, we have used the corresponding GW potentials, which give

602 a better description of high-energy unoccupied states. For GW Fe pseudopotential that treats

603 3s and 3p states as valence states was used. Cut-off energy for the plane wave basis set of 800

604 eV, break condition for electronic SC-loop of 10^{-6} eV and 8×8×1 gamma centred mesh for

605 the model 2a, and 4×4×1 mesh for the model 2e were found to lead to the converged electric

606 field gradients. In all cases, the Fermi-Dirac smearing method with sigma set to 0.03 was

607 used. In addition, all the calculations included support grid for the evaluation of the

608 augmentation charges.

609   The Bader charge density analysis[68] with the implementation of Henkelman and co-workers[69]

610   in VASP code was used to obtain the spin charge density of the periodic structures. The

611   charge-spin density of the cluster structures was obtained using Mulliken population scheme.

612   The atomic spin densities were computed for all cluster and periodic models in order to verify

613   the spin density at the ferric or ferrous Fe site. The Fe spin density in its high and

614   intermediate spins was found to amount to ~4e$^-$ and ~2e$^-$, respectively. Note that in high-spin

615   models, spin-polarisation of C and N sites occurs prior to the increase of spin density on Fe.

616   Therefore, the total spin of each cluster or unit cell model was increased until the spin density

617   on Fe became ~4e$^-$, for which the quadrupole splitting energies were obtained (see

618   Supplementary **Table 5**). This approach differs from our previous study on high-spin ferric

619   models,[33] where the spin-state referred to the total spin of the clusters.

620   The quadrupole splitting energy is computed as the coupling between the nuclear quadrupole

621   moment (Q) the non-spherical nucleus and the principle components V_{ii} ($i=x,y,z$) of the

622   electric filed gradient (EDF) tensor at ^{57}Fe nucleus using the following equation:

623    $\Delta E_Q = \frac{1}{2} eQV_{zz}\sqrt{1 + \frac{\eta^2}{3}}$ (1)

624   Where e is the charge of the electron and the asymmetry parameter η is computed as $=$

625    $(V_{xx} - V_{yy})/V_{zz}$, where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The nuclear quadrupole moment, Q, for $J=3/2$

626   state is taken to be 0.16 barn. Computation of ΔE_Q and η therefore becomes a question of

627   computing the EFG tensor, which is readily obtained as an expectation value of the EFG

628   operator, $V_{ij} = \langle \Psi_0 | \frac{3ij-r^2}{r^5} | \Psi_0 \rangle$, for the electronic ground state Ψ_0 and $i,j=x,y,z$ being the

629   components of the electron radius vector r. For a direct comparison to experimentally

630   reported values, calculated values of ΔE_Q are reported in units of mm·s^{-1}.

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633 **Data availability**

634 The raw data that support the findings of this study are available from the

635 corresponding authors upon request. In particular: The X-ray absorption

636 spectroscopy raw data associated with this work is permanently stored at

637 synchrotron SOLEIL and available upon request; the raw data related to electron microscopy

638 images are permanently stored at LEPMI and available upon request; the raw data related to

639 X-ray radiographs are permanently stored at the APS synchrotron and available upon request;

640 the ^{57}Fe Mössbauer spectroscopy data and the raw and reconstructed tomography data are

641 available at Institut Charles Gerhardt Montpellier and available upon request.

642 **Code availability**

643 The source code used for DFT calculation with deMon2k is available at http://www.demon-

644 software.com/public_html/download.html, upon request for academic purpose. The Vienna

645 Ab Initio Simulation Package (VASP) is a proprietary software available for purchase at

646 https://www.vasp.at/.

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879 **Author contributions**

880 J.L. and F.J. designed and synthesized the materials, and conducted the electrochemical and

881 physical characterizations. M.T.S. and J.L. designed and conducted the *in situ* and *ex situ*

882 Mössbauer spectroscopy measurements. M.T.S. conducted Mössbauer data analysis. A.Z. and

883 J.L. conducted the *operando* and *ex situ* XAS measurements. A.D.C. designed the *operando*

884 fuel cell for XAS. F.J., A.Z., J.L. and J.M.A. conducted the *in situ* XES experiments. I.C.O.,

885 T.M., I.M. and P.A. conducted the DFT computation. K.K., L.D. and F.M. performed TEM

886 and STEM-EDX analyses, G.D. performed atomic-scale STEM analyses, I.Z. and Y.H.

887 performed tomography and TEM analyses. J.L., M.T.S. and F.J. wrote and edited the

888 manuscript with input from all authors. The project was supervised by F.J.

889 **Additional information**

890 Supplementary information is available in the online version of the paper. Correspondence

891 and requests for materials should be addressed to F.J.

892 **Competing interests**

893 The authors declare no competing interests.

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a

exp.
fitted
D1
D2
sextet1
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b

c

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5 h

initial

50 h

e

10 μm
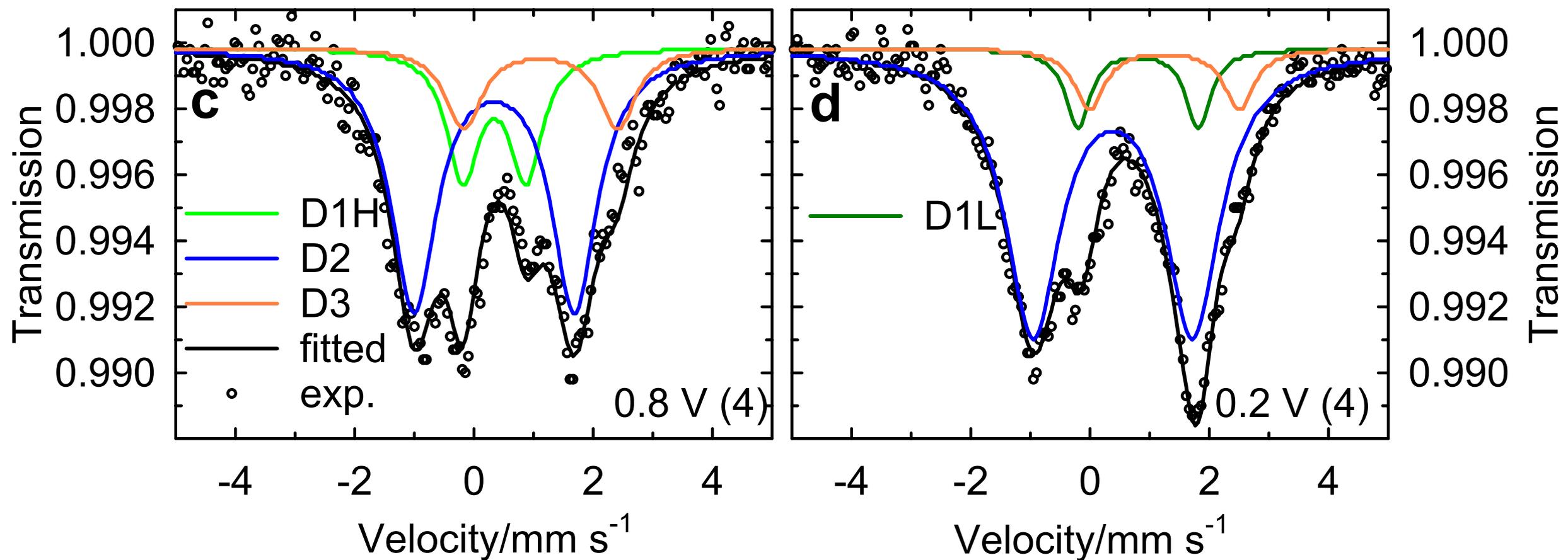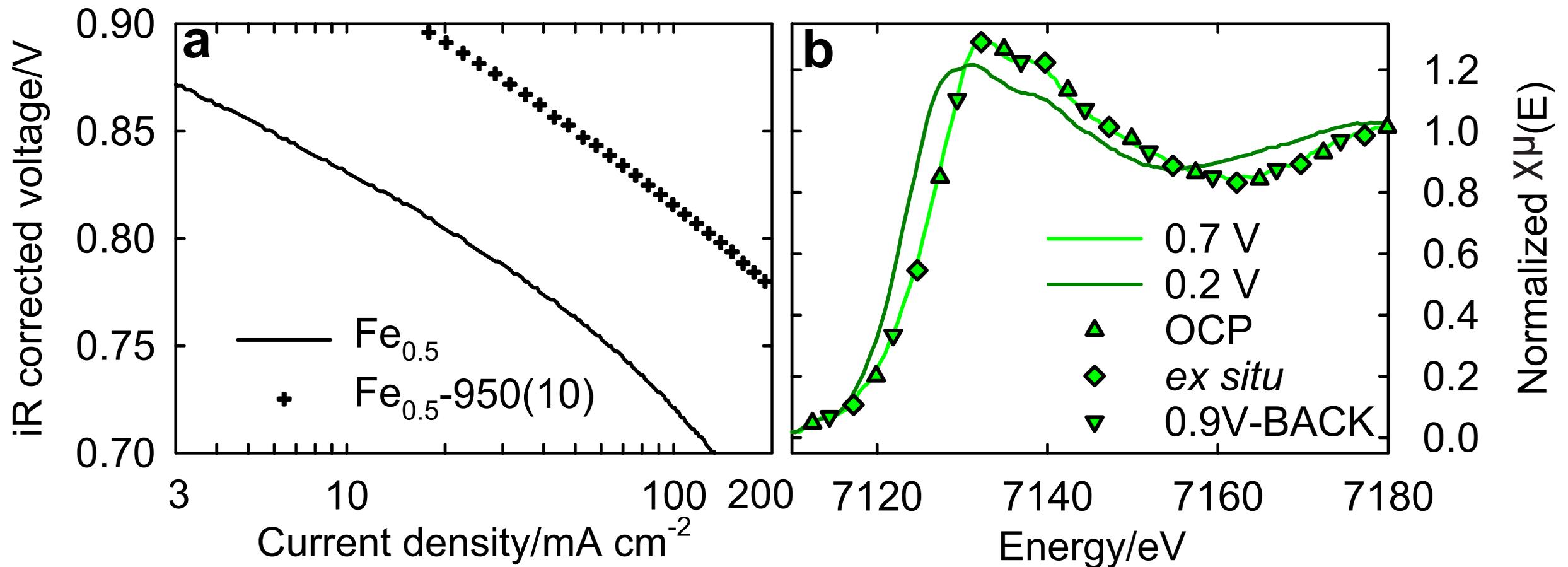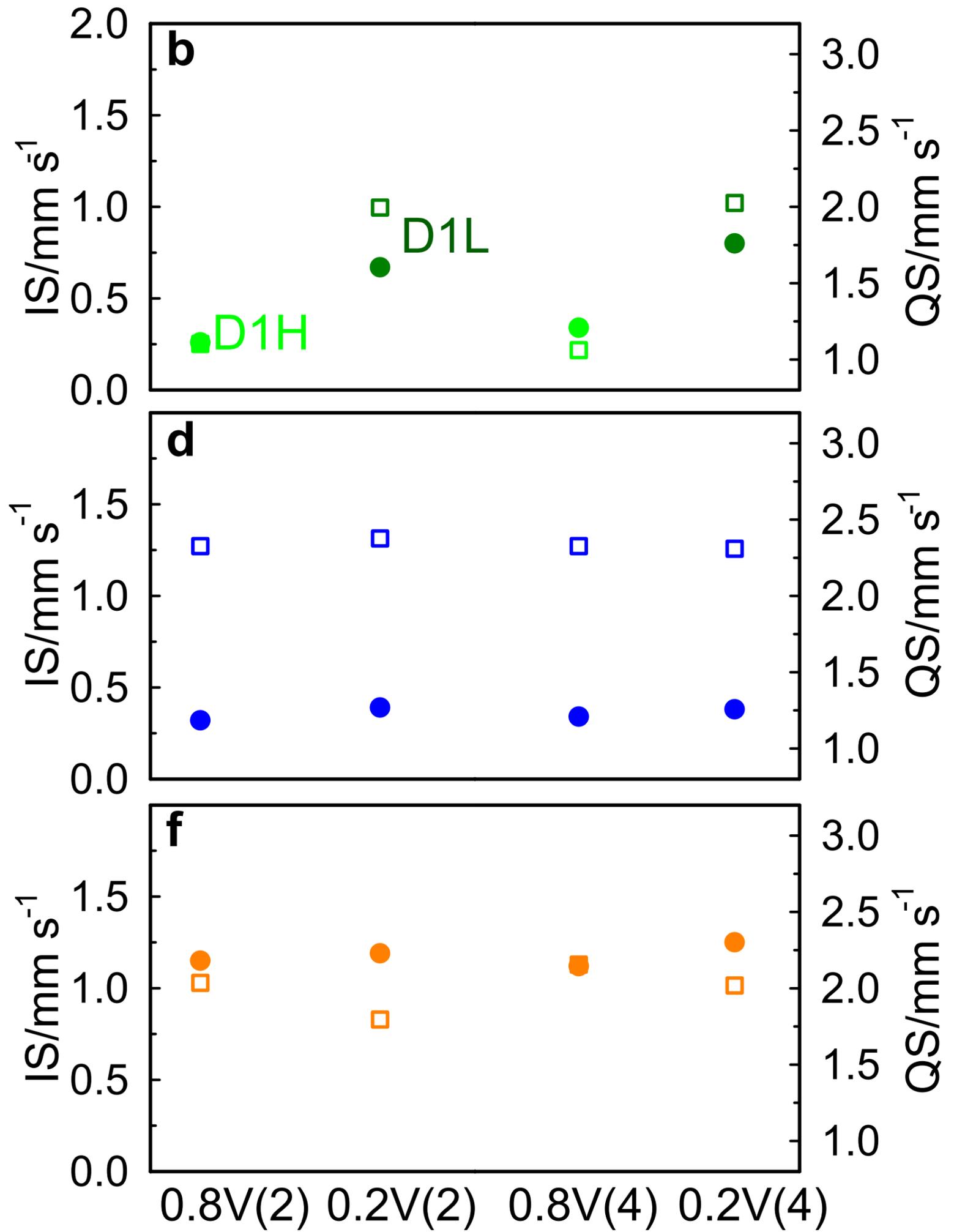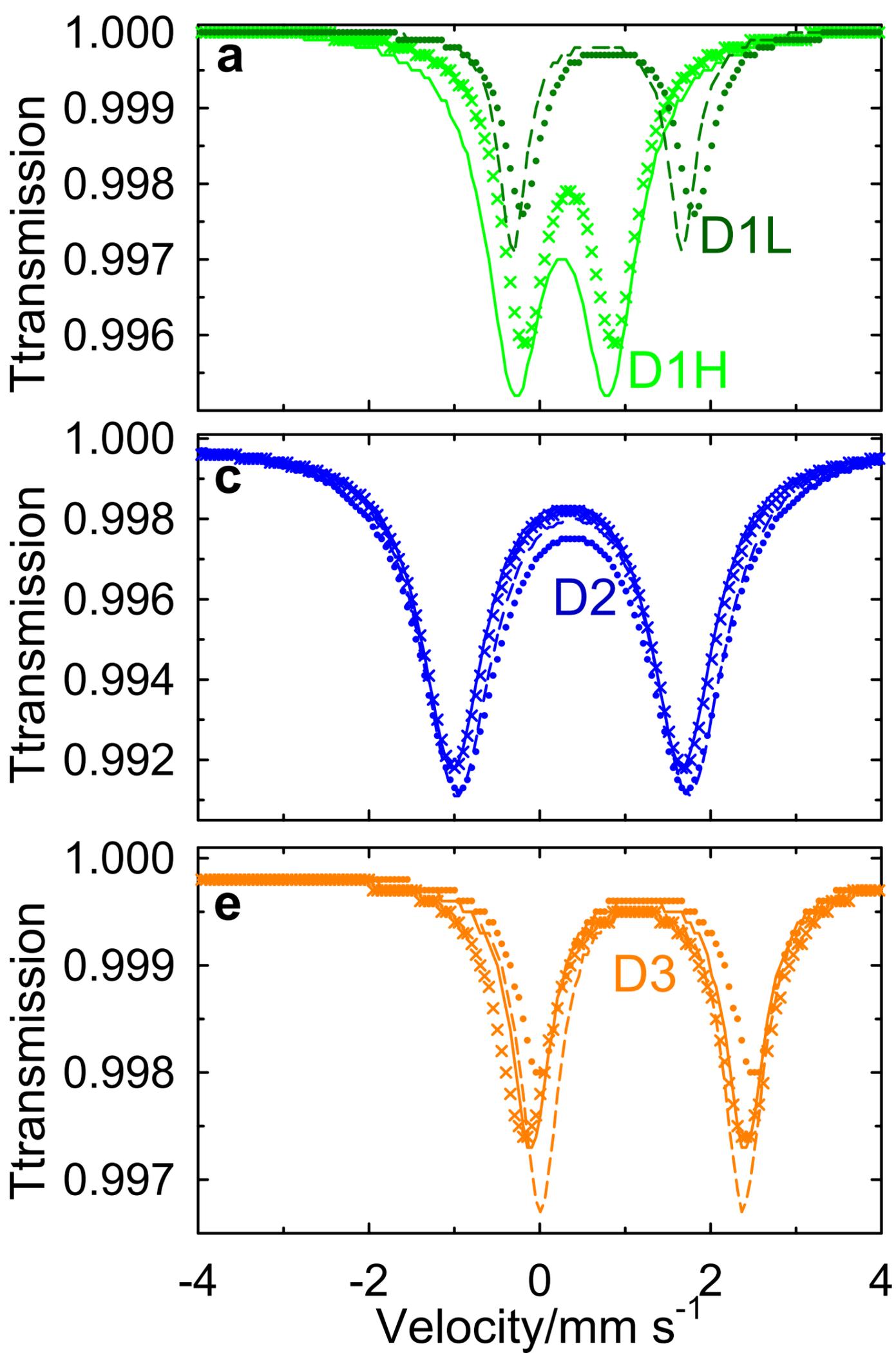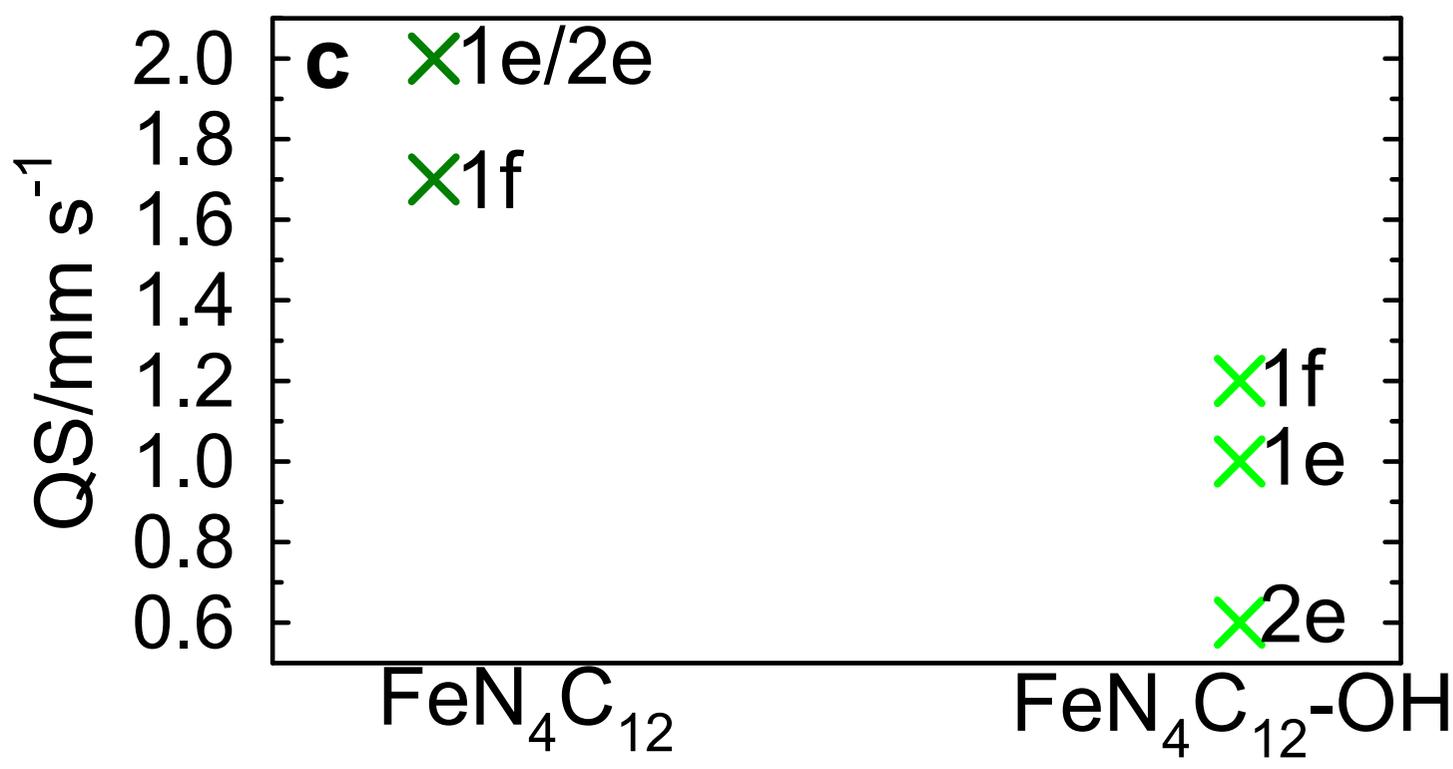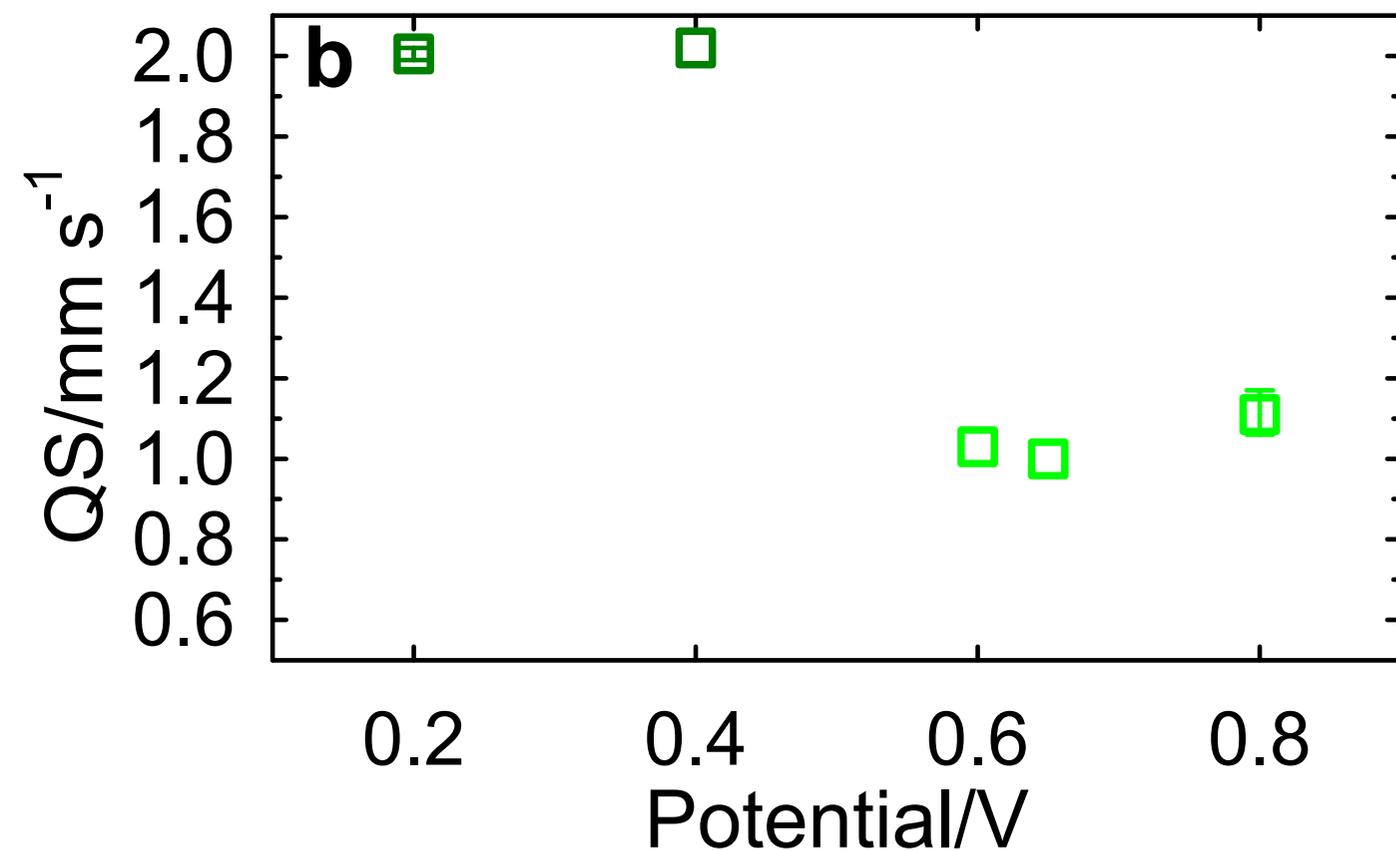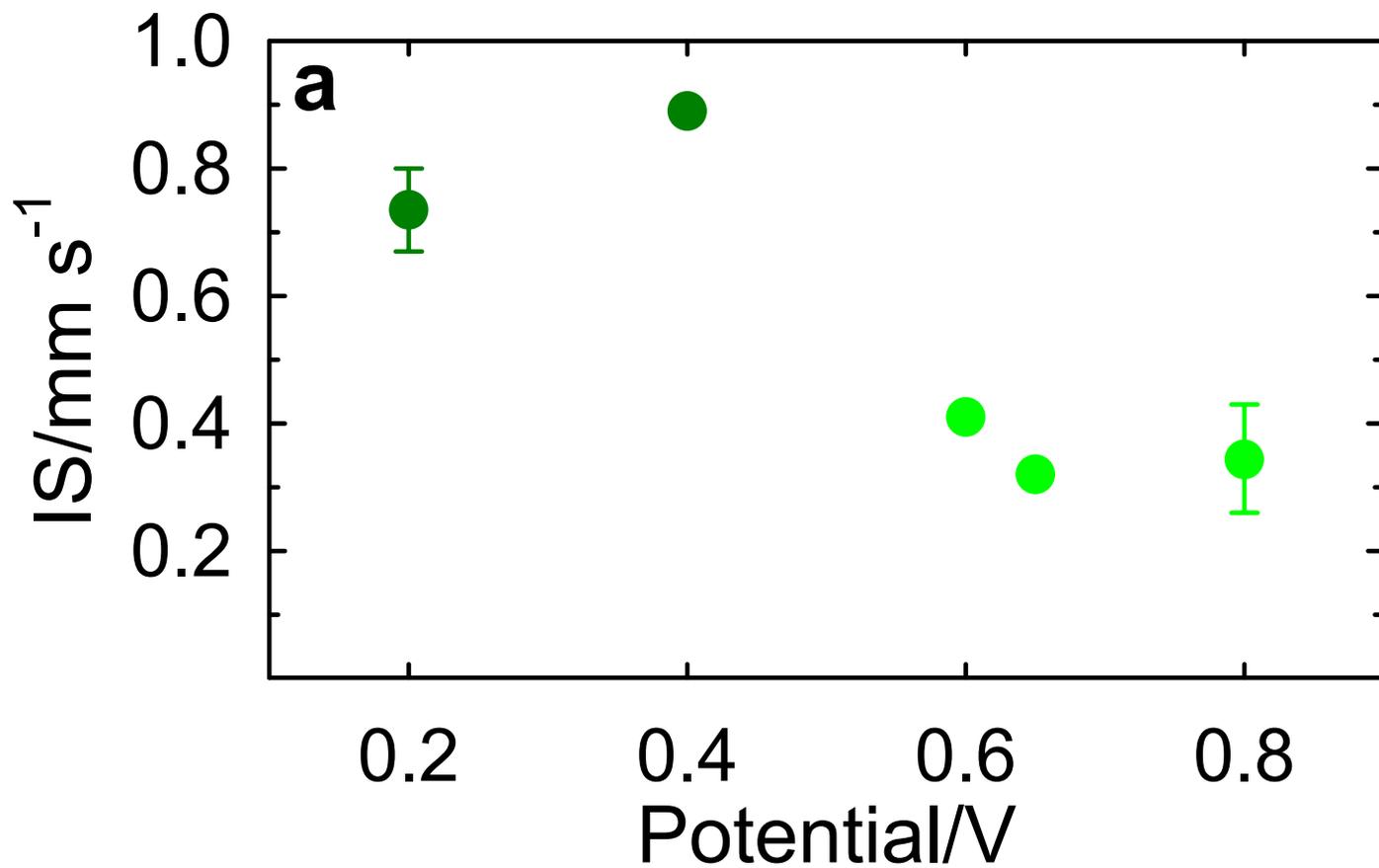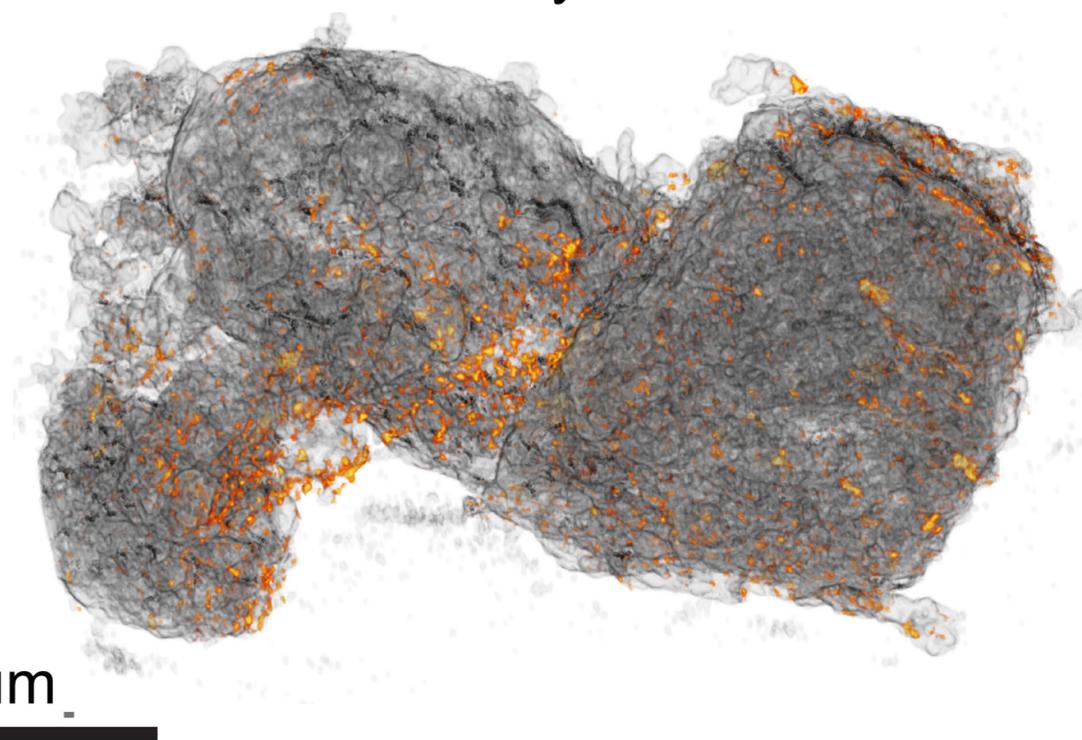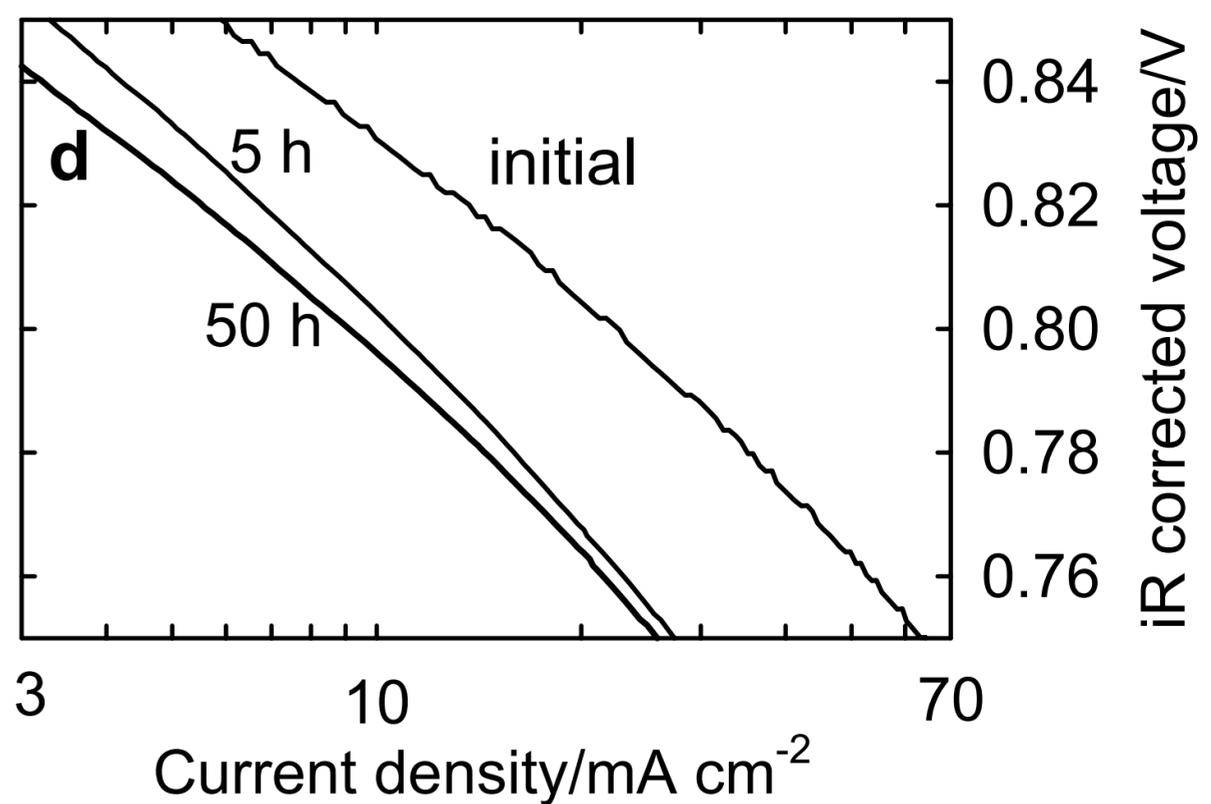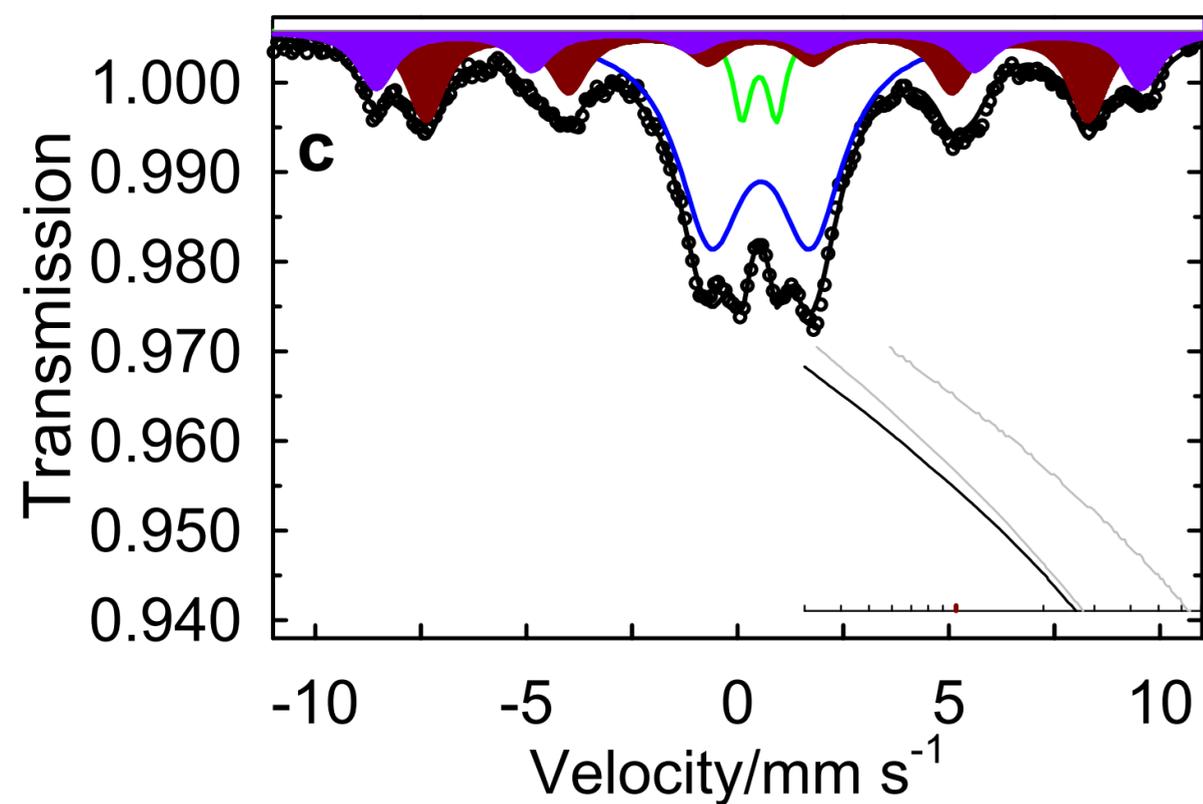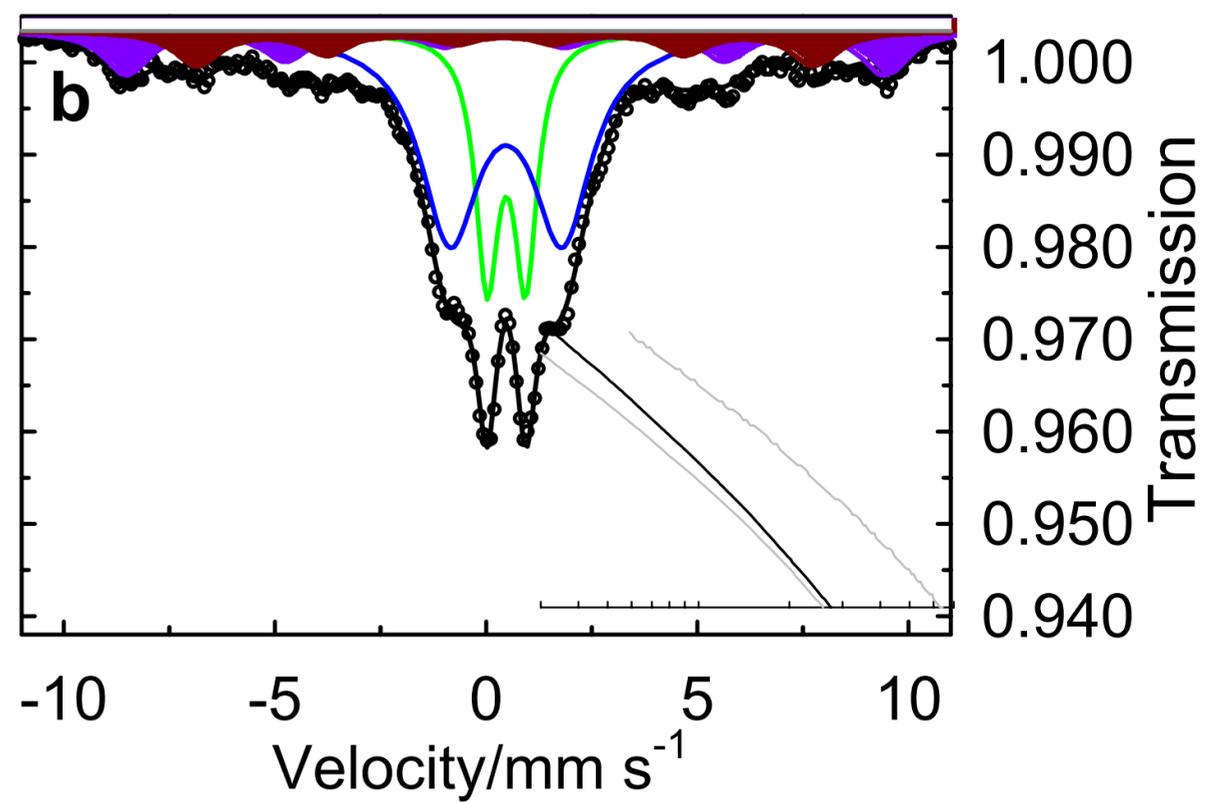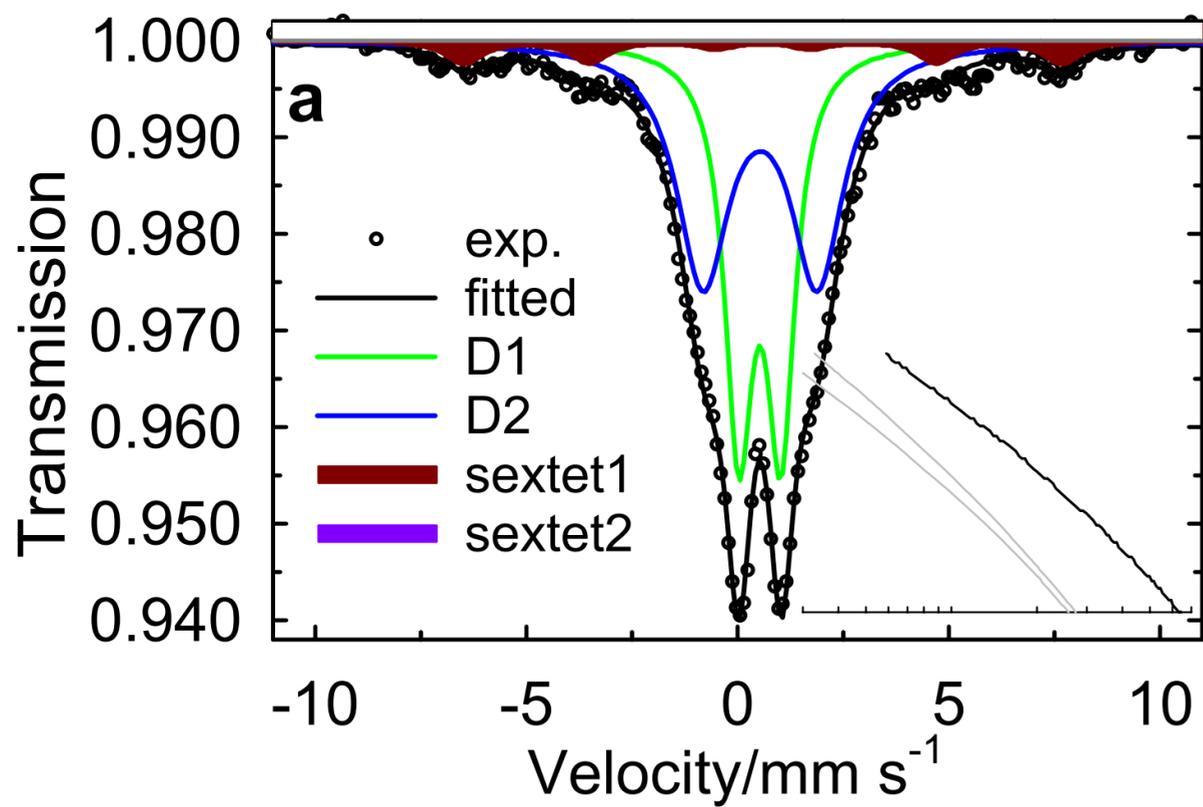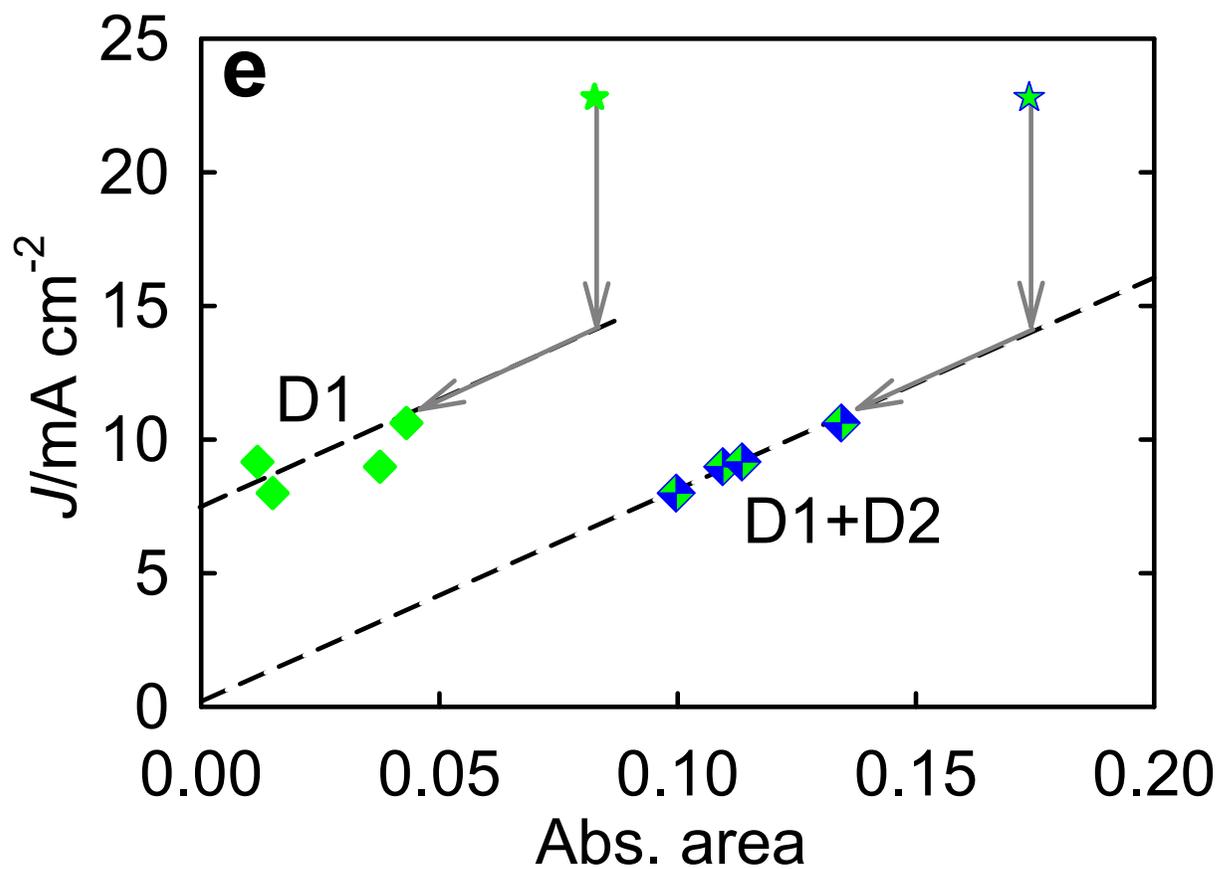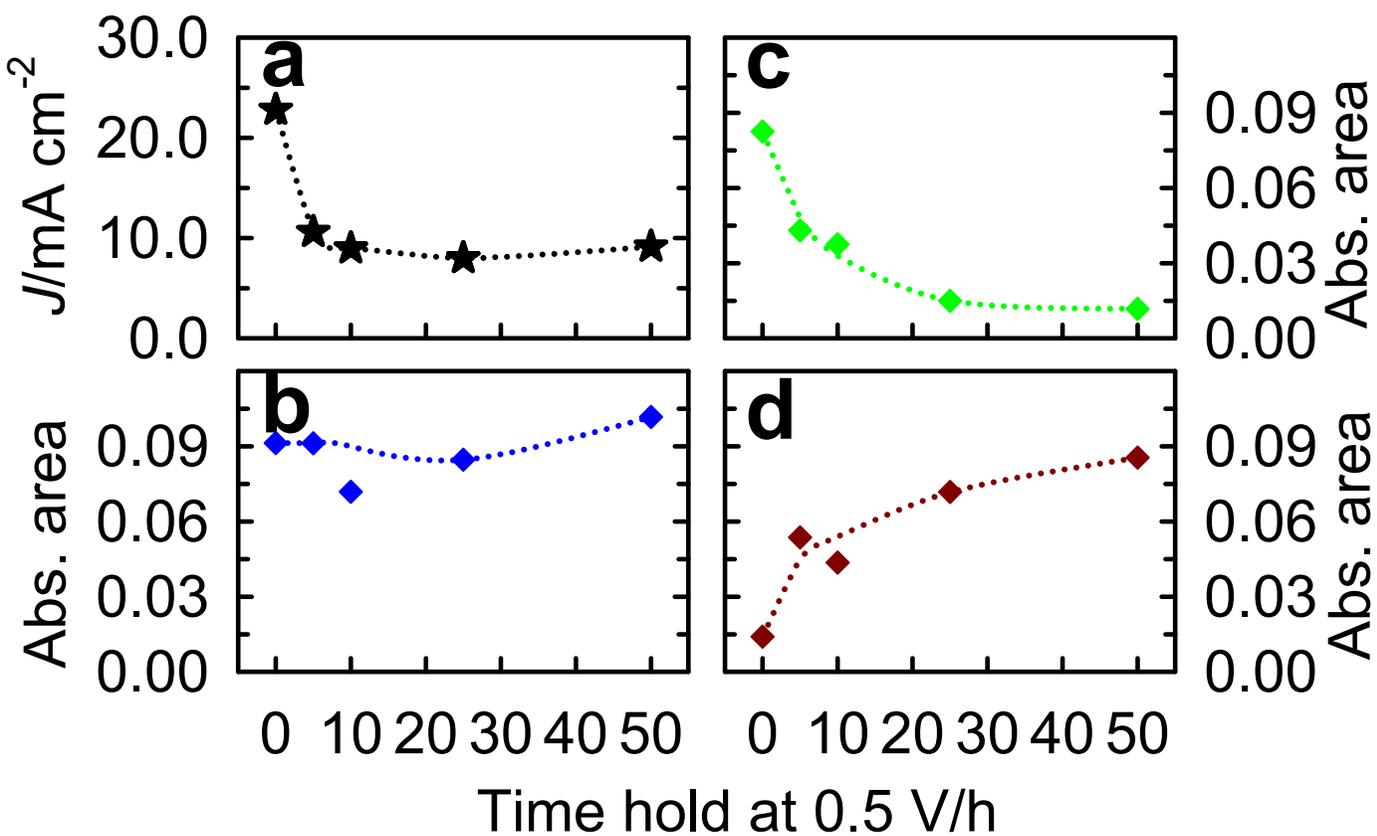
Site S1

D1H (0.8 V/ *ex situ*)

Ar

D3

Expose to air

D1L (0.2 V)

Fe_2O_3 clusters

O_2

Site S2

D2

Ar

D2

O_2

D2

Pristine

Site S2

Site S1

Site S1

Site S2

Transmission

Velocity/mm s⁻¹

After operation

EoT

Fe₂O₃ clusters

Transmission

Velocity/mm s⁻¹

10 µm

Fe$_{0.5}$

a

600 nm

S-4800 x50.0k

Fe$_{0.5}$-950(10)

b

600 nm

S-4800 x50.0k

Fe$_{0.5}$

c

100 nm

Fe$_{0.5}$-950(10)

d

100 nm

Fe$_{0.5}$

e

Intensity

Fe$_{0.5}$-950(10)

f

Intensity

(2θ) 10   20   30   40   50   60

g

1 nm

h

1 nm

i

1 nm

a Pristine (300 K)

D1: high spin Fe^{3+}
IS: 0.3-0.4 mm s^{-1}

b *In situ* (Ar, 300 K)

D3: high spin Fe^{2+}
IS: 1.1-1.2 mm s^{-1}

c EoT (300 K)

Dox: high spin Fe^{3+}
IS: 0.3-0.4 mm s^{-1}
(overlap with D1)

d EoT (5 K)

Sextet: Fe_2O_3

IS: 0.3-0.6 mm s^{-1}

Transmission

Velocity/mm s^{-1}

D1

Fe demetallation

SO$_3$ SO$_3$ SO$_3$ HSO$_3$

D3

Exposed to air

Fe_2O_3 nano-clusters

Fe_2O_3 nano-clusters