### Supplementary Material for

### Electrochemical Fluorination of perovskite type BaFeO<sub>2.5</sub>

Oliver Clemens<sup>a,b,c,\*</sup>, Carine Rongeat<sup>b</sup>, M. Anji Reddy<sup>b,d</sup>, Andreas Giehr<sup>a,b</sup>, Maximilian Fichtner<sup>b,d</sup>, Horst Hahn<sup>a,b,c</sup>

a) Technical University of Darmstadt, Joint Research Laboratory Nanomaterials,

Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany.

- b) Karlsruhe Institute of Technology, Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
- c) University of Birmingham, School of Chemistry, Edgbaston, Birmingham B15
  2TT, United Kingdom.
- d) Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Albert-Einstein-Allee 11, 89081 Ulm, Germany.
  - \* Corresponding Author Fax: +49 6151 16 6335 E-Mail: oliver.clemens@kit.edu

## Some general comments about the Rietveld analysis of multiphase compositions

When refining multiphase compositions, it is highly important to be aware of correlations between the refined parameters. In our case, the reflections of the electrolyte are the most intense reflections in the pattern. Since this electrolyte can be synthesized in its pure form, it is possible to learn structural parameters (see Figure S 1) on the diffraction pattern of the pure phase, and to subsequently use those parameters for the later evaluation of the multiphase mixture.



Figure S 1. Rietveld fit using a structural model of La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (space group *P*-3*c*).

Once those parameters are known, it is also possible to determine other preparational related peak position errors (such as sample height displacement), which are necessary to be known correctly for the fit of the perovskite reflections. If this correction is known, the determination of a cubic lattice parameter would be in principle possible even from one single reflection, however it will be shown later that there is more than one reflection which can be fitted and judged concerning the quality of fit. In addition, we'd like to make the reader aware that reflections at higher angles shift more significantly for changes of the lattice parameter according to Bragg's law than low angle reflections.

The quality of the fit was judged by three ways:

- The R<sub>wp</sub> gives an indication about how much the inclusion of a further perovskite type phase helps to improve the fit. Due to correlation with electrolyte reflections, one needs to be careful since an additional phase might not really help to improve the fit of the reflection profile of the main reflection groups but could also somehow correlate with the electrolyte.

- Therefore, judging the fit of the overall intensity profile and the reliability can be best judged "by eye", and we therefore show several fits using different models on the following pages.
- The difference curve can give a very good indication if there's something wrong with the fit, especially in cases when there is clear deviation from the noise of the measurement.

Furthermore, it might be worth mentioning that it is not possible to refine structural parameters such as occupation factors, atomic positions, O/F ratios etc. from the quality of data. Therefore, we used structural models of a cubic perovskite  $BaFeO_3$  (the exact anion stoichiometry has a very minor influence on the reflection intensity which is of subordinate importance for the fits shown here) and the structural model of  $BaFeO_{2.5}$  as it was published in <sup>1</sup> without refining any of the structural parameters. Even lattice parameters were fixed for the monoclinic  $BaFeO_{2.5}$  phase and the cubic lattice parameter was only refined for the cubic perovskite type phase.

In the main text, we first discuss the cell  $BaFeO_{2.5} II La_{0.9}Ba_{0.1}F_{2.9} II CeF_3$  and discuss the cell  $BaFeO_{2.5} II La_{0.9}Ba_{0.1}F_{2.9} II MgF_2$  afterwards. Since the Supporting Material provided here is meant to show the appropriateness of the fit models used, we have to switch the order in which the cells are discussed, since the type of phases can be easier recognized for the cell with MgF\_2 as the anode.

### About the Rietveld analysis of the cathode site of the charged cell BaFeO<sub>2.5</sub> II La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> II MgF<sub>2</sub>

If one uses only the electrolyte phase to fit the pattern (see Figure S 2), one can see clearly reflections (resp. group of reflections in the angular ranges 30-34, 36.5-40, 44-47, 54-58, 65-68 ° 2 $\theta$ ), which are not described by the intensity profile of the electrolyte phase. Those reflections all belong to the reflections of the perovskite type cathode material and allow for the determination of an average cell volume (i. e. pseudocubic lattice parameter), which is indicative for changes due to oxidation (resp. oxidative fluorination) of BaFeO<sub>2.5</sub>.



Figure S 2. Fit of the charged cell using only the electrolyte phase ( $R_{wp} = 11.651$ ).

If only the monoclinic phase of the starting material as published in <sup>1</sup> (without refining any lattice parameters of the latter) is used to the refine pattern (see Figure S 3), one can see in the difference curve that a broader (nearly) cubic perovskite phase is missing (broad reflections with approximate centers at 31.8, 38.8, and 56.2  $^{\circ}$  20; there is also an reflection indicated at 45.6  $^{\circ}$  20 at the tail of the electrolyte peak). If this phase is cubic or shows a small distortion of the cell symmetry cannot be determined exactly from the quality of data, however, it is clear that the number of reflections is enough to at least roughly determine an average cell volume of this second perovskite type phase (resp. pseudocubic lattice parameter).



Figure S 3. Fit of the charged cell using a model with only the monoclinic perovskite phase of  $BaFeO_{2.5}$  ( $R_{wp} = 8.732$  %).

The fit can therefore be significantly improved by changing to a model with 2 perovskite type phases (i. e. lower number of parameters), one cubic perovskite phase with a ~ 4.040 Å (which is significant for compounds of the BaFe(O,F)<sub>3-d</sub> system containing Fe<sup>4+</sup>) and the second perovskite type phase using the structural model of monoclinic BaFeO<sub>2.5</sub> as published in <sup>1</sup> (again without refining any lattice parameters of the latter). For the use of this model, the difference curve around the main reflection group between 30-34 ° 20 does not show a clear deviation from the noise any more. Also, this model allows to properly refine the intensity pattern of to reflection groups 36.5 – 40 and 54 -58 ° 20. Furthermore, one can clearly see that the amount of this cubic modification is by far not negligible, since it is found in a ratio of ~2:3 in comparison to the monoclinic BaFeO<sub>2.5</sub> phase.



Figure S 4. Fit of the charged cell using a model with the monoclinic perovskite phase of BaFeO<sub>2.5</sub> and another cubic perovskite phase ( $R_{wp} = 7.561$  %). Linear intensity scaling (a) and logarithmic intensity scaling (b).

Alternatively, one could also imagine to use a model with multiple cubic perovskite phases (see Figure S 5). In this case It can be seen that the three main freestanding reflection groups at 30-34, 36.5-40, and 54-58 ° 20 are not fitted correctly concerning their intensity profile, although such a 3 phase model (with independently refined lattice parameters) is very flexible. Especially the main reflection groups at 30-34 and 54-58 ° 20 gives a significant deviation from noise for the difference curve.



Figure S 5. Alternative fit of the charged cell using a model with 3 cubic perovskite phases ( $R_{wp}$  = 7.888 %). Linear intensity scaling (a) and logarithmic intensity scaling (b).

# About the Rietveld analysis of the cathode site of the charged cell BaFeO2.5 II La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> II CeF<sub>3</sub>

As for the cell with MgF<sub>2</sub> as the anode, if one uses the electrolyte phase only to fit the pattern (see Figure S 6), one can see clearly reflections (resp. group of reflections in the angular ranges 30-34, 36.5-40, 44-47, 54-58, 65-68  $^{\circ}$  20. Those reflections all belong to the reflections of the perovskite type cathode material and allow at least for the determination of an average cell volume. This shows there is clearly more than one freestanding reflection to refine the lattice parameter of the perovskite phase reliably on. Furthermore, compared to the cell which was charged against MgF<sub>2</sub>, the intensity distribution of these reflections look far more symmetric with far less expressed shoulders and splitting of the reflections.



Figure S 6. Fit of the charged cell using only the electrolyte phase ( $R_{wp} = 11.482$ ).

Only including a cubic phase with a lattice parameter of ~ 4.02 Å helps to improve the fit significantly (Figure S 7). All the perovskite reflections are then in the right position. There are now two smaller misfits, which can be spotted by investigating the difference curve: The peak at ~  $32^{\circ}$  20 shows a clear shoulder to higher 2 theta values. In addition, a very small further reflection is seen at 55° 20, which should be addressed to improve the fit. The latter very small reflection is significant for monoclinic BaFeO<sub>2.5</sub> (see fits for



Figure S 7. Fit of the charged cell using a model with only one cubic perovskite type phase ( $R_{wp}$  = 8.245 %).

To visualize that the refined lattice parameter is correct, a fit assuming the lattice parameter which would be found for cubic  $BaFeO_2F$  (an  $Fe^{3+}$  containing cubic compound) is shown in Figure S 8 (to visualize it better, scaling parameters and shape parameters were fixed). It can be clearly seen that the order of magnitude of the lattice parameter can be determined correctly, since the positions of those reflections (especially at ~ 38 ° and 58 ° 20) are clearly not right.



Figure S 8. Fit of the charged cell using a model with only one cubic perovskite type phase with a lattice parameter of 4.058 Å.

Including a second cubic perovskite phase gives a fit (see Figure S 9) which is significantly improved. The difference curve at the positions of the perovskite

reflections becomes rather smooth and it can now be seen that no further phases need to be added to describe the pattern appropriately. The lattice parameter of this phase is significantly larger at ~ 4.065 Å (this lattice parameter is in the order of magnitude of phases which contain  $Fe^{3+}$  only, see main article) and the lattice parameter of the main cubic perovskite phase decreases further to ~ 4.017 Å. However, it can be seen that the very small peak at 55° 20 is not described ideally with this second phase.



Figure S 9 Fit of the charged cell using a model with two cubic perovskite type phases ( $R_{wp} = 7.943$  %).

If the fit is performed using the structural model of monoclinic BaFeO<sub>2.5</sub> ( $P2_1/c$ ) as the second phase, the R<sub>wp</sub> value is essentially the same compared to a fit using two perovskite type phases with the same lattice parameter. However, the peak at 55° 20 is now in the right position. The cubic perovskite phase is now being refined with a lattice parameter of 4.022 Å, which is significant for phases containing Fe<sup>4+</sup>, and the refinements clearly show that the main perovskite phase is refined reliably. Since the quality of fit cannot be distinguished comparing the models of (a) a second cubic perovskite phase or (b) BaFeO<sub>2.5</sub> as the second phase, one should probably prefer speaking about "an Fe<sup>3+</sup> containing fraction" from the analysis of the lattice parameter. However, from the similarity to the cell which was charged against MgF<sub>2</sub> (see Figure S 3) for which the BaFeO<sub>2.5</sub> modification can be clearly seen, we think that the assumption of is at least chemically plausible.



Figure S 10. Fit of the charged cell using a model with two cubic perovskite type phases ( $R_{wp} = 7.948 \%$ ).

#### Air tightness of the cell

The cell was tested to be air tight by leaving it for 3.5 days under the same conditions than used for charging (150°C, sealed). The pattern below shows a fit using the structural model as published in <sup>1</sup> (only refining lattice and shape parameters). The lattice parameters do not change significantly, and the cell volume (respectively pseudocubic lattice parameter of 4.075 Å) are basically identical. This confirms that oxidation from air impurities are unlikely under the applied conditions.



Figure S 11. Cathode site of a cell heated in the sealed cell used at 150 °C without applying voltace for 3.5 days.

### The monoclinic perovskite type compound observed for heating samples of composition BaFeO<sub>2.5-x/2</sub>F<sub>x</sub> under nitrogen

When heating the compound under nitrogen (and also under air) we observed the formation of another vacancy ordered perovskite compound. Indexing of the reflections indicated a monoclinic space group with lattice parameters of a = 10.1252(3) Å, b = 5.7080(1) Å, c = 6.9859(2) Å, and beta = 92.806(2) °. Rietveld fits could be performed by structural subgroup transformation of a cubic perovskite into the space groups  $P2_1/m$  and P2/m with the lattice parameters given above (which both resulted in a reasonable fit, see Rietveld fit for the use of space group  $P2_1/m$ ). However, we'll elaborate the exact kind of vacancy order in more detail and will report about the crystal structure together with a structural discussion in an independent article. The exactness of the determination of the cell volume (resp. pseudocubic lattice parameter of  $a_{pseudocubic} \sim 4.066$  Å) is not affected by potential smaller errors in the anion position and confirmed by independently performed Pawley fits.



Figure S 12. Rietveld analysis of a new vacancy ordered perovskite modification using a space group model of  $P2_1/m$ . The increasing background intensity results from the use of a variable divergence slit and the high fluorescence of Fe.

### **References:**

1. O. Clemens, M. Gröting, R. Witte, J. M. Perez-Mato, C. Loho, F. J. Berry, R. Kruk, K. S. Knight, A. J. Wright, H. Hahn and P. R. Slater, *Inorg. Chem.*, 2014, 53, 5911-5921.