

Local and correlated studies of humidity-mediated ferroelectric thin film surface charge dynamics:

Supplementary Materials

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Supplementary Method 1: Complete humidity-sample-time dataset

The complete humidity-sample-time dataset is shown in Supplementary Figure 1, for the two samples (up and down polarised) and ten humidities.

Supplementary Method 2: Data stacking principle

The 660 acquired KPFM contact potential difference images have been stacked in a single data cube with dimensions 10240 x 512 x 33. The first stacking was performed along the x dimension, with each image being 512 x 512 pixels, and at each time point there being measurements on two samples at ten humidities each. The second stacking was performed along the z direction (or time axis), with the 33 time points.

The idea behind this stacking method is described in our previous work¹ and yields time-dependent behaviours which are common to all parameters stacked along the x/y dimensions: humidity, nature of sample, and space. This ensures that time-dependent behaviours can be compared across humidity and between the two samples simultaneously and quantitatively.

Supplementary Method 3: Spectral decomposition principle

The principle behind spectral decomposition methods such as DictionaryLearning is shown in Supplementary Figure 2. The complete dataset is split into a set of one-dimensional components with corresponding two-dimensional weight maps. Dimensional stacking was used to integrate the relative humidity and initial sample polarisation dependence into the maps, thus correlating the data sets and enabling quantitative comparison of time-dependent decays.

Supplementary Note 1: Dependence on the number of components

A systematic investigation of the influence of the number of components on the DictionaryLearning analysis is shown in Supplementary Figure 3. As the number of components increases, so does the number of physical behaviours. At first, when $n = 2$, only a single physical behaviour is visible, alongside a Gaussian noise component with a null weight map. When the number of allowed components is increased up to $n = 6$, the negative voltage process splits from the main component. Increasing the number of components to $n = 7$, the concentric structure for the negative voltage region starts to form with the split of the latter into two distinct map/component pairs. At $n = 8$, a background component splits from the positive voltage component, and finally at $n = 10$, a third concentric negative component makes its appearance.

Supplementary Note 2: Reaction-diffusion modeling

The reaction-diffusion modeling, here based on a Fitzhugh-Nagumo excitation-relaxation process, provides insight into the contribution of the various physical processes to the machine learning based analysis. Such a sandbox approach enables a unique way to tailor the interactions present within the two species. In particular, the reaction-diffusion modeling highlights the importance of sparse approaches such as DictionaryLearning when dealing within physical materials presenting very different co-located behaviors.

Initial conditions choice

Initial species distributions were chosen to mimic the positive and negative charges as deposited by biased-tip atomic force microscopy writing. The positive charge species u shown in Supplementary Figure 4(a) was initialized with only a reaction interaction with the negative charge species v , and no diffusion component. The negative charge species v , shown in Supplementary Figure 4(b) is susceptible to both reaction and diffusion processes. The total distribution $u - v$ is shown in Supplementary Figure 4(c), and qualitatively resembles the Kelvin probe force microscopy data in Main Figure ??.

Principal component analysis

Whilst principal component analysis (PCA) does not provide a physically interpretable spectral decomposition, it can be used to estimate the complexity of the decomposition. The PCA weight maps for the first 50 components are shown in Supplementary Figure 5(a), illustrating the concentric-like pattern generated by the diffusive nature of the negative charge species distribution v . Indeed, the positive charge species distribution u is only present in the first four maps of the decomposition. The corresponding

PCA components shown in Supplementary Figure 5(b) additionally shows a periodic behaviour with increasing frequency for the first 26 components, as evidenced by their Fourier transform in Supplementary Figure 5(c).

Non-negative matrix factorization

A non-negative matrix factorization (NMF) approach was tried concurrent to DictionaryLearning, with results for $n = 4$ and $n = 10$ components shown in Supplementary Figure 6(b,c) respectively. Although not able to separate the physical processes as cleanly as DictionaryLearning, NMF also highlights the concentric decomposition of the negative voltage species with an increasing number of components.

Supplementary Note 3: Classical statistical analysis

The main advantage of the machine learning approach is its mathematical objectivity, which can be used to untangle multiple behaviours that are present within the dataset without human intervention. Whereas without it we have to rely on manual area selection, the spectral decomposition algorithm enables us to impartially identify behaviours that are correlated through the two samples and ten humidities.

When manual data analysis is performed, three main challenges arise. First, area selection for further analysis is an ambiguous and non-objective process. Our human nature will guide a pattern-based selection, which in the case of the dataset under study in this work is challenging, as there is spatial evolution of the CPD signal distribution as a function of humidity. Second, even if regions of interest are selected as parsimoniously and unambiguously as possible, there is a spatial gradient throughout the data set, which contributes to the loss of accuracy in any subsequent analysis. Finally, encompassing the above two reasons, any behaviour extracted from manual averaging will be correlated and intermixed with those of neighbouring zones.

An example of manual analysis is presented in Supplementary Figure 7, where the regions of interest were selected based on the initial writing pattern, and kept the same for both samples and all ten humidities. As the analysis was performed on each sample/humidity set of control conditions separately, direct comparison beyond the visual inspection or fitting of each individual curve (as was done in²) is challenging.

Supplementary Note 4: Current-voltage during voltage application

In the standard tip-sample-electrode geometry of scanning probe microscopy measurements, the asymmetry of the electrodes strongly favors the emission of electrons from the tip. This may have an influence on the surface charge distribution as a function of humidity.

Figure 8 shows the currents recorded on the up- and down-polarized samples at low (10%RH) and high (70%RH) humidity during voltage application similar to the writing. Additionally, current-voltage characteristic curves were recorded on a grid spanning the written areas. As can be seen in Supplementary Figure 8, at high humidity both samples display large currents during the application of negative voltages, corresponding to field emission from the tip, with the higher humidity enabling

a better tip-sample contact. Very little current is visible overall both during writing and sweeps on the up-polarized sample, indicating a higher sample quality with less defects and leakage.

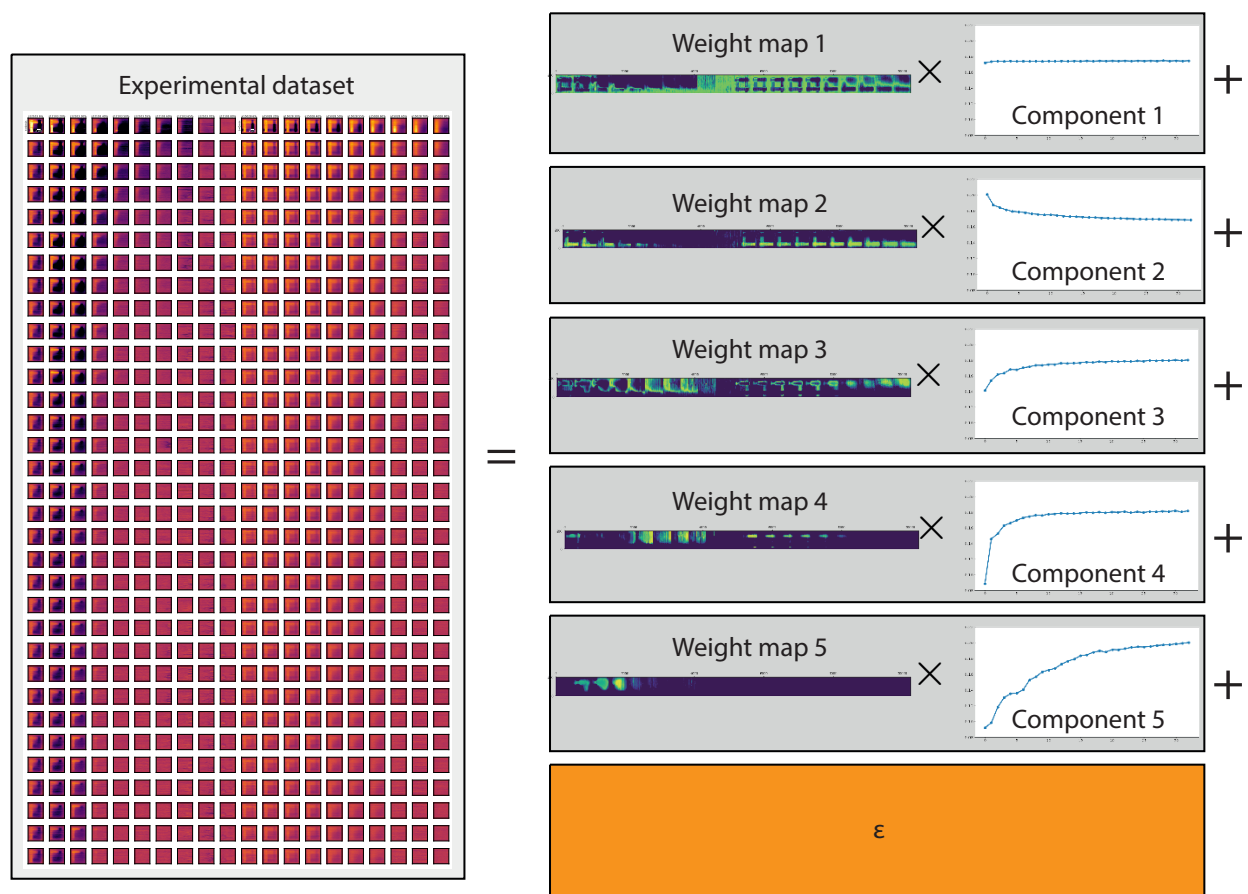
These results are consistent with past measurements performed on PZT thin films of the same composition, where only domain walls were found to have steady-state conductivity.^{3,4}

References

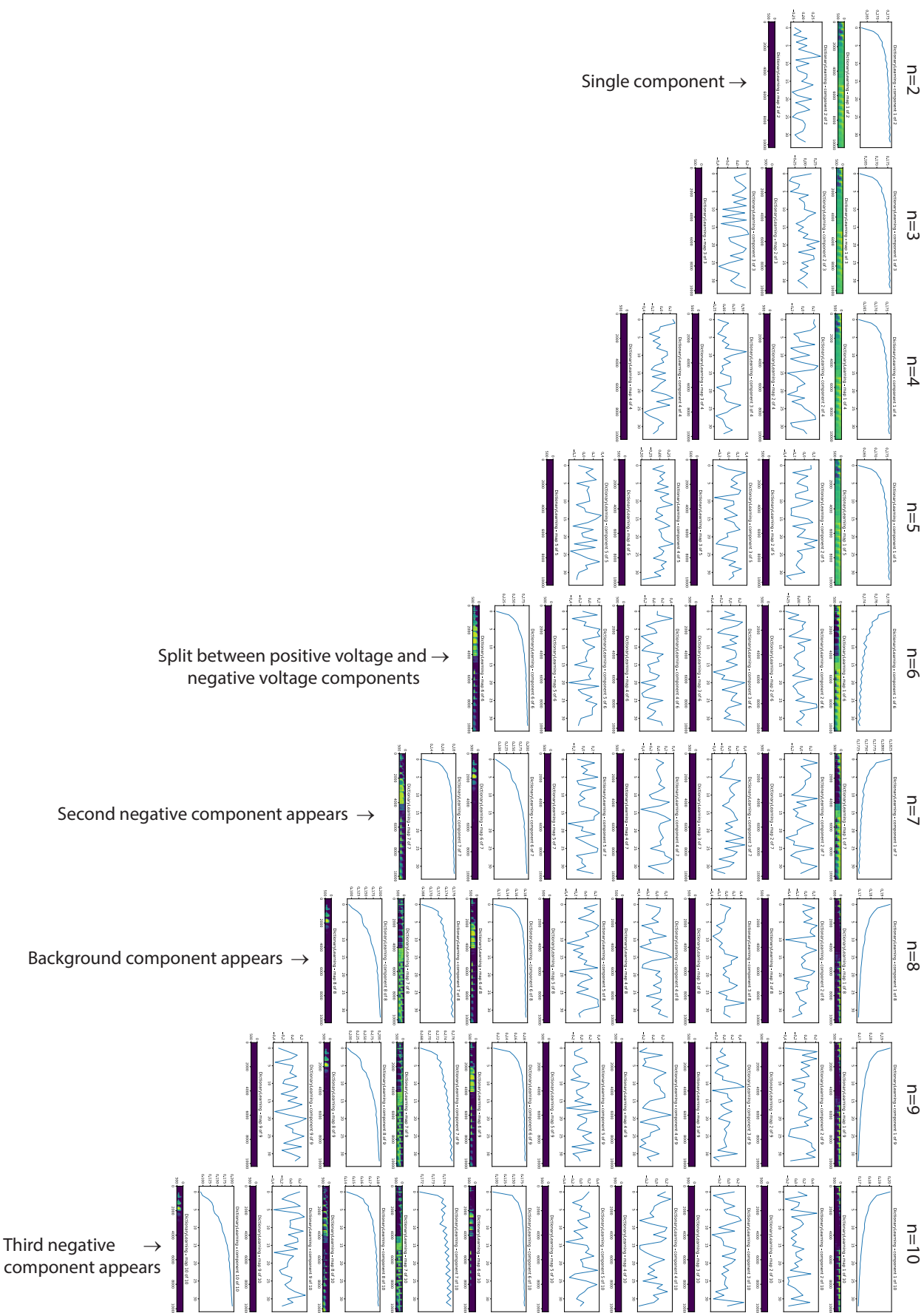
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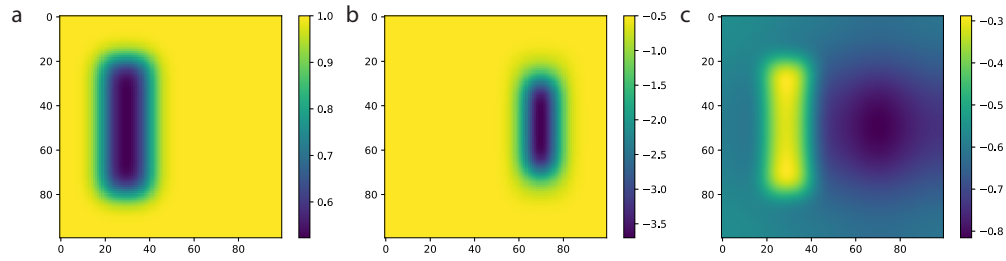
Supplementary Figure 1. Complete KPFM contact potential difference dataset as a function of sample, relative humidity and time.



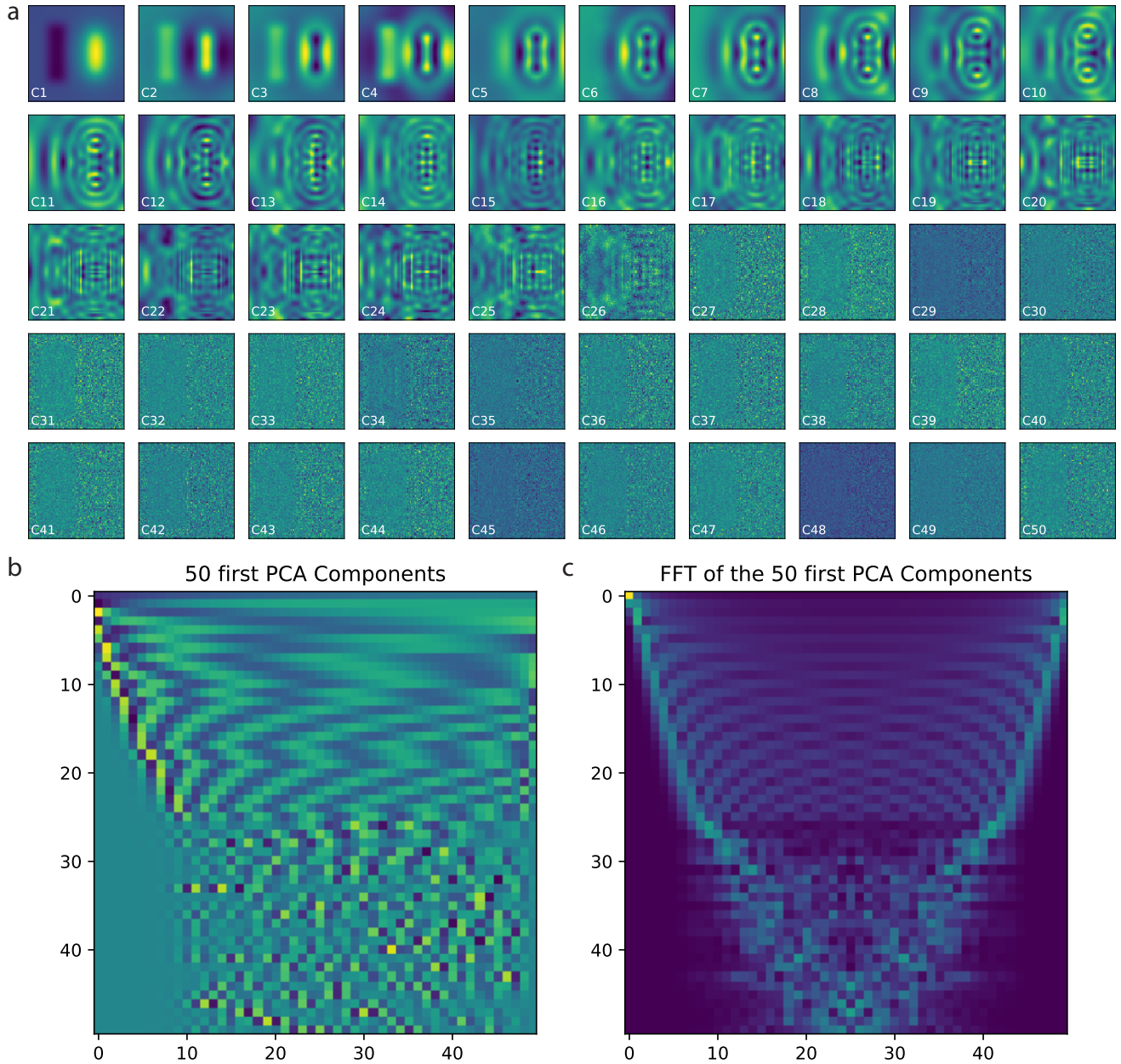
Supplementary Figure 2. Principle behind machine learning based spectral decomposition.



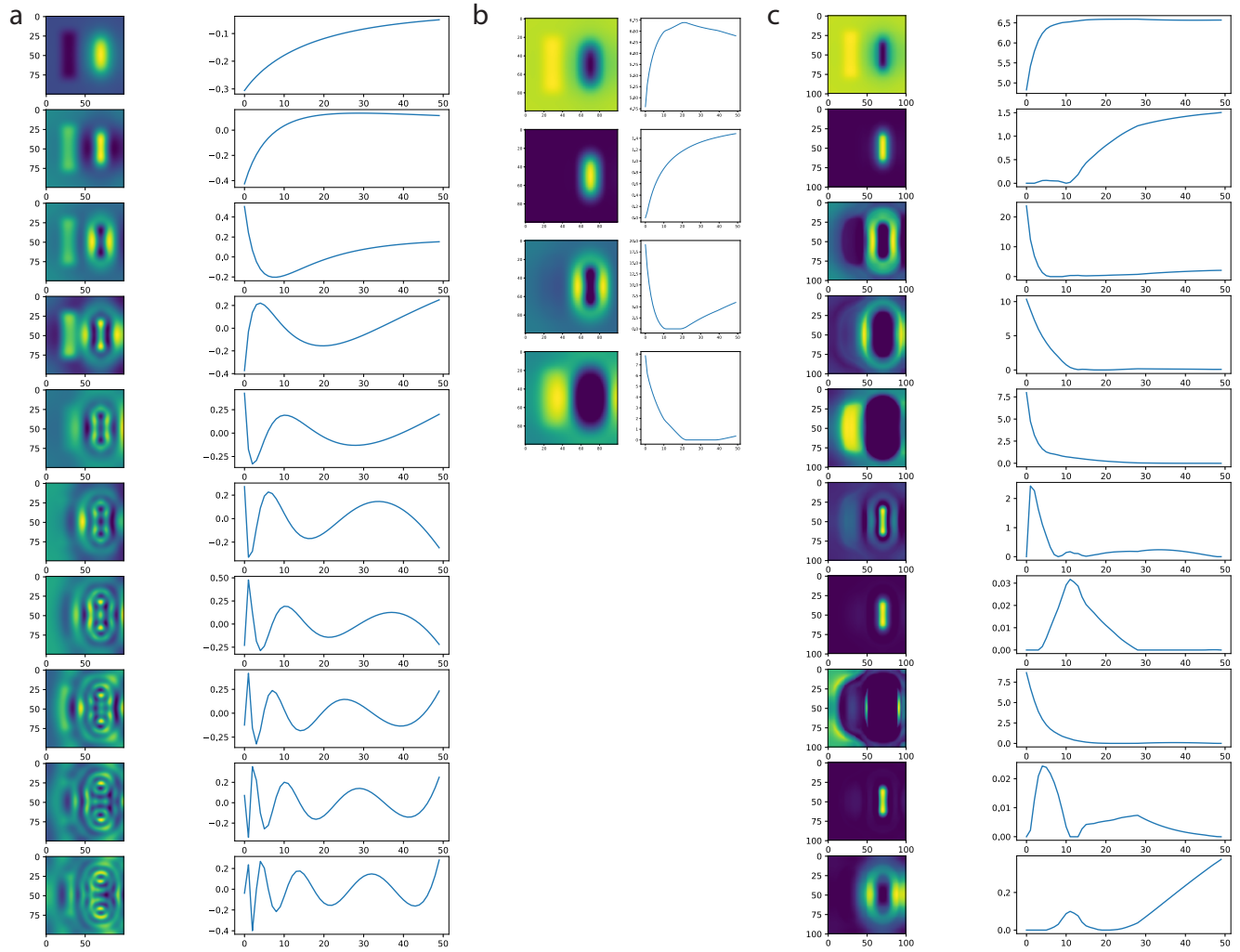
Supplementary Figure 3. Dictionary Learning based spectral decomposition of the correlated KPFM contact potential difference dataset as a function of the number of components. Increasing number of components refines the separation into further sub-processes.



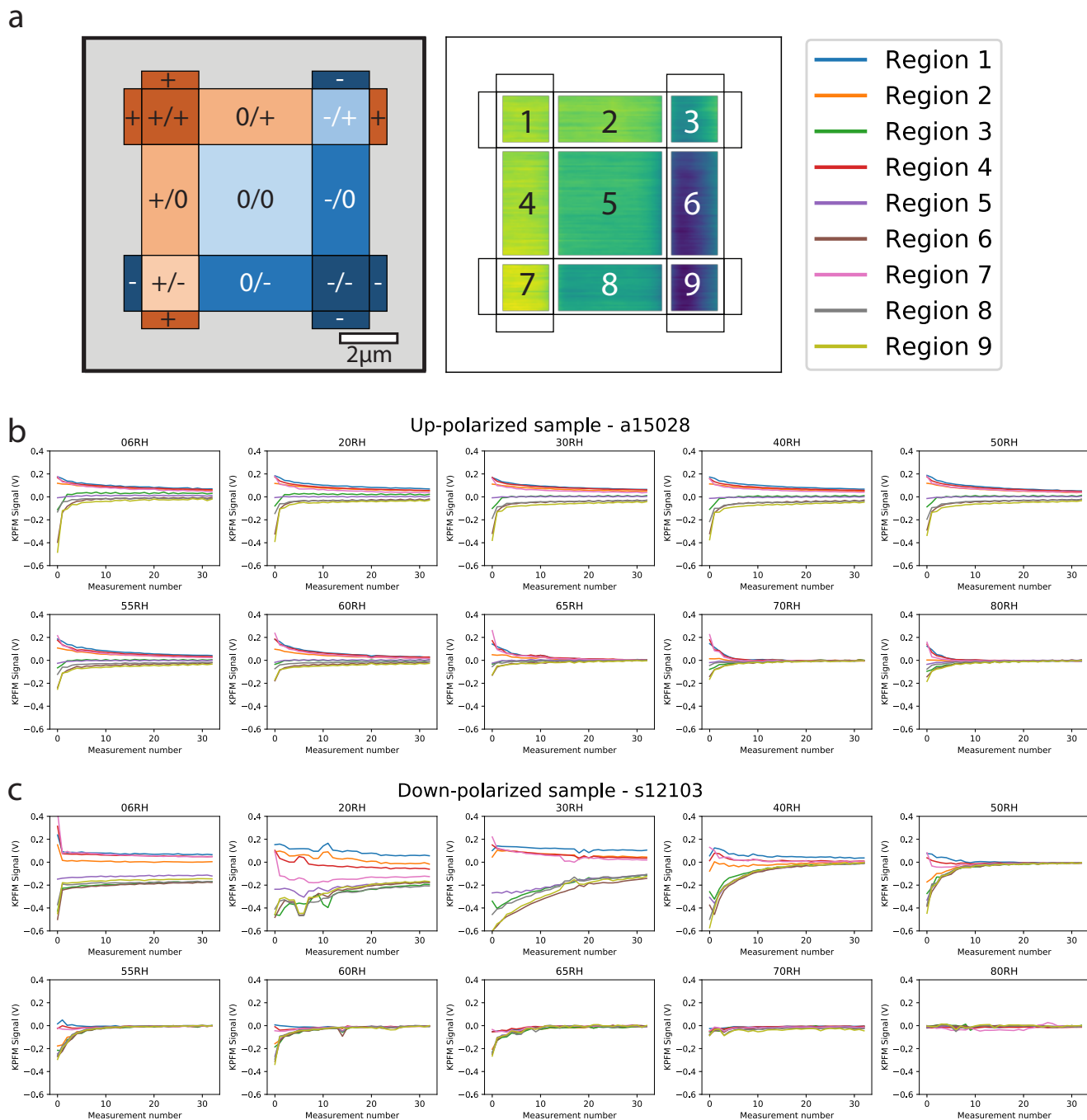
Supplementary Figure 4. Initial distributions of the two reacting/diffusing species (a) u and (b) v . The resulting potential is computed in (c) as $u - v$ and processed further with machine learning techniques.



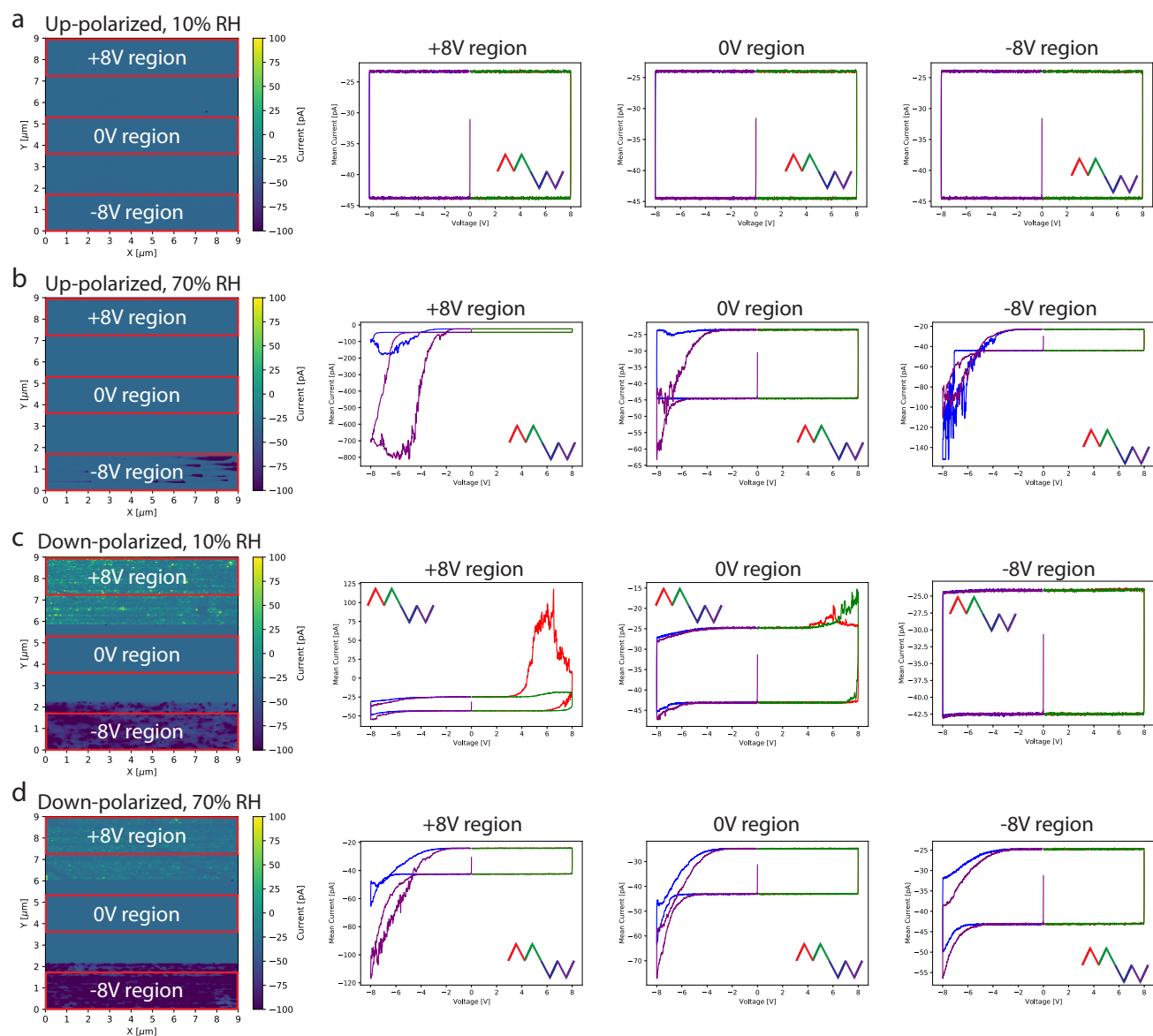
Supplementary Figure 5. Principal component analysis of the reaction-diffusion dataset up to 50 components, with (a) the maps and (b) their corresponding components. (c) The Fourier transform in the components shows an increasing oscillation frequency for the increasing order components.



Supplementary Figure 6. Comparison between PCA (a) and NMF (b) $n = 4$ and (c) $n = 10$ methods. In all cases - just like in the DictionaryLearning analysis - the negative voltage species generate concentric components due to their diffusive nature.



Supplementary Figure 7. Classical statistical analysis of the time-dependent CPD signal decay for the two samples and ten humidities. (a) Schematic of the writing pattern and the corresponding nine regions of potentially different behaviours selected to minimize intermixing. (b) The up-polarized and (c) down-polarized sample results, with each graph representing the time evolution of the average signal within the nine regions.



Supplementary Figure 8. Currents observed during writing and current-voltage characteristic curves for voltage ramps on the written areas for the up- and down-polarized samples at low (10%RH) and high (70%RH) humidity. The current-voltage characteristic curves are displayed after averaging the result of a PUND-like spectroscopic acquisition on a grid.