Electric nanogenerators that directly convert the energy of moving drops into electrical signals require hydrophobic substrates with a high density of static electric charge that is stable in “harsh environments” created by continued exposure to potentially saline water. The recently proposed charge-trapping electric generators (CTEGs) that rely on stacked inorganic oxide–fluoropolymer (FP) composite electrets charged by homogeneous electrowetting-assisted charge injection (h-EWCI) seem to solve both problems, yet the reasons for this success have remained elusive. Here, systematic measurements at variable oxide and FP thickness, charging voltage, and charging time and thermal annealing up to 230 °C are reported, leading to a consistent model of the charging process. It is found to be controlled by an energy barrier at the water-FP interface, followed by trapping at the FP-oxide interface. Protection by the FP layer prevents charge densities up to –1.7 mC m$^{-2}$ from degrading and the dielectric strength of SiO$_2$ enables charge decay times up to 48 h at 230 °C, suggesting lifetimes against thermally activated discharging of thousands of years at room temperature. Combining high dielectric strength oxides and weaker FP top coatings with electrically controlled charging provides a new paradigm for developing ultrastable electrets for applications in energy harvesting and beyond.

1. Introduction

In search of clean and renewable energy sources, so-called (tribo)electric nanogenerators that convert mechanical energy into electrical energy have recently attracted substantial attention.$^{[1–16]}$ The efficiency of triboelectric nanogenerators is, however, limited by the relatively small$^{[1,6–9,11–14]}$ and often unstable$^{[5,7,8,15]}$ and poorly controllable$^{[5,15,17–19]}$ surface charge density generated by triboelectrification. Achieving large and stable charge densities by controlled injection (or ejection) of charge carriers into a material by various methods$^{[20]}$ was studied before in the context of electrets: (quasi-)permanently charged materials that are ubiquitous because of their use in the majority of (consumer) microphones,$^{[20–22]}$ as nowadays commonly used in smartphones. Suitable materials require a high dielectric strength and good insulation properties,$^{[20]}$ and should be hydrophobic to avoid discharging due to ambient humidity.$^{[21–26]}$

The same conditions apply to dielectric materials in electrowetting-on-dielectric (EWOD) applications.$^{[27,28]}$ In EWOD, these conditions are often satisfied by using composite dielectrics that consist of an insulating, high dielectric strength inorganic layer coated with a hydrophobic fluoropolymer (FP) layer.$^{[27–33]}$ Contrary to electrets, charge injection is undesirable in electrowetting as it leads to contact angle saturation.$^{[29,32,34–40]}$ Recently, however, it was demonstrated that this effect, which is preferentially localized near the three-phase contact line due to local field enhancement$^{[34,43]}$ can also be transformed into a useful processes denoted as electrowetting-assisted charge injection (EWCI) to create well-defined localized charge patterns of high charge density.$^{[42]}$ As a modification of the process, homogeneous EWCI (h-EWCI) that suppresses the contact line singularity of the electric field and involves a dielectrically stable oxide layer underneath a hydrophobic fluoropolymer film, subsequently enabled charge densities of the order of ~1 mC m$^{-2}$ and higher that were homogeneous over cm$^2$ areas (h-EWCI), stable over ≥100 days under ambient conditions, and showed no appreciable degradation under the impact of (highly saline) droplets.$^{[31,16]}$ (High stability could only be achieved for negative charging polarity.$^{[42]}$) Notwithstanding these substantial improvements compared to conventional triboelectric nanogenerators as well as corona-based charging of electrets, the mechanisms behind the h-EWCI process, the origin of the long-term stability, as well as the parameters to optimize it even further have so far remained elusive.
In this work, we therefore systematically vary the design of our composite FP–inorganic electret materials and characterize their charging and discharging behavior: we fabricate samples of variable oxide- and polymer thickness, charge them by h-EWCI at variable (negative) voltage up to complete dielectric breakdown, and subsequently assess the stability of the injected charge carrier upon annealing up to temperatures of 230 °C. We find an ultrastable and high effective surface charge density of \(-1.7 \text{ mC m}^{-2}\) that can be injected in a controlled manner. Based on a model that we derive to describe the charging and relaxation process, we attribute the stable and high effective charge density to the combined effect of a high-dielectric strength, well-insulating inorganic (silicon) oxide layer, and deep penetration of charge carriers through the protecting hydrophobic FP layer.

2. Results

2.1. Charging Composite Electrets

We prepared a series of composite samples consisting of highly p-doped Si wafers with thermally grown oxide layers of thickness \(d_{\text{ox}} = 30 \text{ nm}...3.6 \mu \text{m}\) that were covered by spin coating with thin layers of FP (Teflon AF 1600) with a thickness \(d_{\text{p}} = 300 \text{ nm}...1.1 \mu \text{m}\) (see Figure 1 and the Experimental Section for details). The samples were charged using the h-EWCI process, as developed earlier.\[13\] In short, an adhesive tape with a 1 cm\(^2\) opening was applied to the sample surface as a mask to define the surface area to-be-charged. Subsequently, a large puddle of aqueous NaOH solution \((1 \times 10^{-3} \text{ m})\), wider than the opening in the mask, was deposited on the sample and a charging voltage \(U_C\) was applied for charging periods \(\tau_C\) of 2 min to 4 h between the silicon wafer and a Pt wire immersed into the puddle. The polarity of the aqueous phase was negative such that negatively charged (hydroxyl) ions are attracted toward the FP surface. Over finite values of the surface potential \(U_0\), it was found to depend on the charging time, as shown in the inset of Figure 2b (see discussion further below). In the limit of low charging voltages (i.e., \(|U_C| < |U_{\text{min}}|\), we found small but finite values of the surface potential \(U_0 = (\pm 10 \pm 5) \text{ V}\) (such that \(U_0 \ll U_C(|U_C| > |U_{\text{min}}|)\)). On the basis of separate tests with hundreds of impinging drops (Figure S1, Supporting Information), we tentatively attribute this small \(U_0\) to slide/triboelectrification, as described earlier by others.\[19,43–45\] In the opposite limit, for high charging voltages, the appearance of bubbles indicated dielectric breakdown and electrolysis beyond a critical voltage \(U_{\text{BD}}(d_{\text{ox}}, d_{\text{p}})\).\[36\] (In fact, the thickest sample types turned out to be stable up to the highest charging voltage of \(U_C = -815 \text{ V}\) available in our setup.) These observations can thus be summarized in the following empirical relation

\[
U_S = \alpha(\tau_C) \cdot (U_C - U_{\text{min}}) \quad \text{for } |U_{\text{min}}| < |U_C| < |U_{\text{BD}}|
\]

\[
U_S = U_0 \quad \text{for } |U_C| \leq |U_{\text{min}}|
\]

with \((d_{\text{ox}}, d_{\text{p}})-\text{dependent values of } U_{\text{min}}, U_{\text{BD}}\), and \(U_0\). Beyond \(U_{\text{min}}, a \text{ (charging time-dependent) fraction } \alpha \text{ of the charging voltage is thus "converted" into a surface potential. In the}

![Figure 1](https://www.afm-journal.de)

**Figure 1.** Charge injection mechanism, with a) drift of negatively charged ions to the surface, b) charge carrier transfer to the dielectric layer, and c) injected charges remaining in the dielectric after removal of the voltage and the droplet, resulting in surface potential \(U_S\). d) Top view of the charging setup with contact line protected by polypropylene tape, and e) photo of the charging setup. f) Generated current multiplied with load resistance (blue: 470 k\(\Omega\); red: 810 k\(\Omega\); yellow: 1.67 M\(\Omega\); \(\tau_C = 15 \text{ min}\)). Bottom-left inset: generated current. Top-right inset: mechanism of current generation upon droplet impact.
Charge injection into the FP layer requires a threshold than the value of the applied charging voltage: governed by the local electric fields within each material rather than the location and density of these injected charge carriers (as commonly implicitly assumed in slide/trioboelectric charging), a continuous distribution within the polymer layer, and an accumulation at the polymer–oxide interface are all conceivable and can be important as a reference to compare to other charging methods such as triboelectric- and corona charging, where the polymer surface truly is the location of the trapped charge—see further below.)

Figure 2b shows the effective surface charge $\sigma_{\text{eff}} = U_0 c_0$ as a function of $E_{P,0}$. $\sigma_{\text{eff}}$ is the equivalent surface charge density that generates $U_0$, assuming that it would be located at the polymer surface. (While we will show below that the actually injected amount of charge is different and that it is located at the FP–oxide interface, the value of $\sigma_{\text{eff}}$—which is independent of the penetration depth—is still of interest as a reference to other charging methods such as triboelectric- and corona charging, where the polymer surface truly is the location of the trapped charge—see further below.)

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Breakdown of the full sample at $U_C = U_{BD}$ occurs when the breakdown electric field of silicon oxide is exceeded. Treating the sample as a stack of dielectric materials, the initial electric field in the FP layer ($E_{P,0}$) upon applying the charging voltage prior to any charge injection is

$$E_{P,0} = \frac{U_C}{d_{\text{eff}}} = \frac{U_C}{\varepsilon_0 d_{\text{eff}}} = \frac{U_C}{\varepsilon_0 (d_{\text{eff}} + d_p)} = \frac{U_C}{\varepsilon_0}$$

with the dielectric constants of silicon oxide and FP, $\varepsilon_0 = 3.9$ and $\varepsilon_p = 1.93$, and the equivalent capacitance of the sample $c_0 = (d_{\text{eff}}/\varepsilon_0 + d_p/\varepsilon_p)^{-1}$. Combining Equations (1) and (2) gives

$$U_{SD} = \frac{U_C}{\varepsilon_0} \left| |U_{SD}| + |E_{BD}| \right|$$

The fact that $\alpha$ is substantially smaller than unity is remarkable. It implies that the electric field within the FP layer can become substantially larger than $E_{BD,P}$ upon charging at voltages $|U_C| > |U_{min}|$. We treat this aspect in more detail in Section 3. For the moment, we only note that $\alpha$ is found to depend on the charging time $r_0$ and increases from 0.10 ($r_0 = 10^4 \mu s$) to 0.24 ($r_0 = 4 h$) for the charging times studied here (see inset Figure 2b and Figure S2 in the Supporting Information). The increase appears to be logarithmic i.e., $U_C = A \cdot \log (r_0/r_0)$, as fitted with $A = 0.15$ and an onset timescale for charge trapping $r_0 = 30 s$, in qualitative accordance with literature on contact angle relaxation in electrowetting. Extrapolating this behavior suggests that $\alpha (r_0)$ relaxes toward 1 (corresponding to an electric field of $E_{BD,P}$ in the FP layer) only for extremely long charging times of $\approx 10^4 \mu s = 3$ years.

Having established that the onset of charge injection is indeed determined by $E_{BD,P}$, we now return to the question of the vertical distribution of injected charge in the sample. Following our assumptions given above, we expect breakdown of the full sample to occur when the electric field in the silicon oxide layer reaches the corresponding breakdown field $E_{BD,OX}$. The electric field in the silicon oxide layer during charging is a linear combination of the field caused by the charges in the droplet ($E = (U_C - U_0) c_0/\varepsilon_0 d_{\text{eff}}$, and the field caused by the injected charges (Figure 3a,b); the latter, however, depends on
the so far unknown vertical distribution of injected charges and therefore allows to discriminate between competing scenarios of charge distribution within our stacked electret sample. To do so, we consider the two limiting cases: in scenario I, all injected charge resides at the aqueous–FP interface (Figure 3a); in scenario II, all injected charge resides at the FP–oxide interface (Figure 3b). In case I, the electric field in the silicon oxide layer is given by \( E_{\text{ox}} = \frac{U_c}{\varepsilon_{\text{ox}} \varepsilon_0} \) and the corresponding charge density \( \sigma = U_c \varepsilon_{\text{ox}} \varepsilon_0 \) is located at the aqueous–FP interface, with a fraction \( \alpha \) injected into trapped states at the FP surface and a fraction \( (1 - \alpha) \) reversibly accumulated in an electric double layer on the liquid side of the interface.

In scenario II, a charge density \( \sigma^\text{II} = U_s \varepsilon_{\text{ox}} \varepsilon_0 \) resides at the FP–oxide interface and the corresponding electric field in the oxide layer is

\[
E_{\text{ox}}^\text{II} = \frac{U_s}{\varepsilon_{\text{ox}} \varepsilon_0} + \frac{U_c - U_s}{d_\text{ox} + d_p} \frac{\varepsilon_{\text{ox}}}{\varepsilon_0} = \frac{\alpha \tau_c (U_c - E_{\text{BD,ox}} d_p) + (1 - \alpha \tau_c) U_c d_\text{ox}}{\varepsilon_{\text{ox}} \varepsilon_0} \tag{4}
\]

This field is stronger than \( E_{\text{ox}}^I \) for the same \( U_s \) because the injected charge is closer to its counter charge on the bottom electrode, which also implies that \( \sigma^\text{II} > \sigma^I \). Equating the expressions for \( E_{\text{ox}}^I \) and \( E_{\text{ox}}^\text{II} \) to the known electric breakdown field of silicon oxide, \( E_{\text{BD,ox}} = -400 \ldots -600 \text{ MV m}^{-1} \) [48] thus results in predictions for the breakdown voltage \( U_{\text{BD}} \) for each combination of \( (d_\text{ox}, d_p) \) for the two competing scenarios of charge distribution, with the one for scenario II always being weaker than the one for scenario I. Comparison to the experimental data for several combinations of oxide and FP thickness clearly favors scenario II with all injected charges accumulating at the FP–oxide interface (see Figure 3c,d). Since any intermediate continuous charge distribution throughout the FP film would fall in between these two limiting scenarios, we can actually conclude from the experimental data that the physically realized distribution must indeed be very close to scenario II. Note that this distribution is very different from corona charging and slide/triboelectrification, where charge has been demonstrated or generally assumed to reside at or near the FP–air interface [2,3,5,19,51]. In a typical corona setup, charge carriers get accelerated in the gas phase by an electric field between the corona tip and a grid but slow down very quickly upon penetrating into the condensed sample phase due to inelastic collisions. In h-EWCI, however, (injected) charge carriers are continuously subject to a very strong electric field because the applied voltage during charging drops between the liquid and the electrode on the substrate, i.e., over a distance given by the sample thickness.

Knowing the charge distribution, we are now in the position to calculate the expected breakdown voltage based on the sample design \( (d_\text{ox}, d_p) \) and the breakdown fields of both materials. Combining Equations (3) and (4), we find

\[
U_{\text{BD}} = d_\text{ox} \left( E_{\text{BD,ox}} + E_{\text{BD,F}} \right) \frac{\alpha \tau_c d_p}{d_\text{ox}} \left( \frac{1 + \frac{d_\text{ox}}{d_\text{ox} \varepsilon_0}}{1 + \frac{d_\text{ox} \varepsilon_0}{d_\text{ox} \varepsilon_0}} \right) \tag{5}
\]

Note that \( U_{\text{BD}} \) is not completely determined by the sample properties but decreases with increasing \( \alpha \) and thus with...
increasing charging time \( \tau \). This conclusion is qualitatively consistent with the experimental observation that higher voltages can be applied for a short time without occurrence of bubbles; only as the charging time is increased, bubbles start to appear.

Using Equations (3) and (5), we can finally predict \( \sigma_{\text{eff}}(=U_S \varepsilon_0) \) as a function of \( U_C \), \( d_{\text{ox}}, d_P \), and \( \alpha \), as in Figure 3e–h, and find good agreement between the modeling results and our experimental data. (Corresponding predictions for \( U_S \) and for the interlayer charge \( \sigma^I \) are shown in Figures S3 and S4 in the Supporting Information.) In particular, the model correctly reproduces the boundaries of the slide/triboelectrification regime at low voltage (white line) and the breakdown regime (red line) at high voltage with the well-controlled h-EWCI regime (color scale). Moreover, the modeled effective surface charge in the h-EWCI regime is in good agreement with the measured effective surface charge (both indicated by the color (gradient)).

2.3. Thermal Stability of the Electret

Being able to model and control the charging of the surface, we now turn to the stability of the surface potential. Following common procedures in electret characterization,[20] we measured the surface potential in various stages of thermal annealing of our samples. Figure 4 shows the surface potential after consecutive steps of annealing for 15 min at annealing temperatures \( T_a = 100, 150, 200, \) and \( 230 °C \). On this timescale (15 min per step), we observed only a minor decay of the surface potential at \( T_a \leq 150 °C \). (Some initially very weakly charged samples even displayed a slight increase in \( U_S \), which we tentatively attribute to slide/triboelectrification caused by the drop impingement during the measurement.) The surface potential of all samples decreased at \( T_a \geq 200 °C \). Yet, even at \( T_a = 230 °C \), i.e., substantially above the glass transition temperature of the polymer (\( T_g \) (AF 1600) = 160 °C)[49] at which the charge of conventional polymer electret materials quickly relaxes, a substantial fraction of the initial surface potential \( U_{S,0} \) is still present. Comparing the initially highly charged samples, we observed that the relaxation is weaker for samples with (relatively) thick oxide layers; while \( U_S \) decreased to 40–50% of \( U_{S,0} \) for samples with \( d_{\text{ox}} = 300 \) nm (Figure 4a,b), more than 70% of the initial surface potential remains after the final annealing step at \( 230 °C \) for samples with \( d_{\text{ox}} = 3.6 \) μm (Figure 4c,d).

To assess the long-term stability of the surface potential, we subsequently annealed our samples at \( 230 °C \) for up to 100 h. The inset of Figure 5 shows the normalized surface potential for various samples initially charged to \( U_{S,0} = -34 \ldots -62 \) V. Like in Figure 4, we find a characteristic decay time that increases with increasing \( d_{\text{ox}} \); e.g., for \( d_{\text{ox}} = 300 \) nm, the surface potential decayed to half of its initial value within 1 h; for \( d_{\text{ox}} \geq 2 \) μm, the same decay took up to 48 h. Interestingly, the surface potential decay is not affected by \( d_P \) above the oxide layer (e.g., \( d_{\text{ox}} = 300 \) nm, \( d_P = 300 \) nm or 1 μm). This observation is consistent with our interpretation above that the injected charge carriers reside at the FP–oxide interface. Moreover, this conclusion implicitly suggests that the charge relaxation is indeed governed by the oxide layer.

To describe the dynamics of the charge relaxation process through the oxide layer, we consider the transit time of charge

![Figure 4](image.png)

**Figure 4.** Surface potential after consecutive annealing at the indicated temperature for 15 min at each step for increasingly negative \( U_C \) from bottom to top in each panel. a) \( d_{\text{ox}} = 0.3 \) μm, \( d_P = 1.0 \) μm, b) \( d_{\text{ox}} = 0.3 \) μm, \( d_P = 0.3 \) μm, c) \( d_{\text{ox}} = 3.6 \) μm, \( d_P = 1.0 \) μm, and d) \( d_{\text{ox}} = 3.6 \) μm, \( d_P = 0.3 \) μm. (Error bars indicate the standard deviation of the surface potential from nine measurements using three different load resistors on a single sample).

![Figure 5](image.png)

**Figure 5.** Inset: Normalized surface potential after annealing for the indicated time at \( T_a = 230 °C \). Main figure: The same data with the time axis normalized by the initial electric field and the oxide thickness, following Equation 6. (Error bars indicate the standard deviation of the normalized surface potential from nine measurements using three different load resistors on a single sample).
carriers through a dielectric layer exposed to an electric field. For an oxide layer of thickness $d_{\text{ox}}$, this transit time via a thermally activated hopping process is given by

$$t_0 = \frac{d_{\text{ox}}}{\mu_{\text{ox}} E_{\text{in}}} = \frac{d_{\text{ox}}^2}{\mu_{\text{ox}} U_0}$$

(6)

Here, $\mu_{\text{ox}}$ is the trap-modulated mobility of charge carriers.\(^2\) Figure 5 shows the normalized surface potential as a function of time normalized by $d_{\text{ox}}$ and $E_{\text{in}}$, from which we estimate $\mu_{\text{ox}} = 5 \cdot 10^{-17}$ m$^2$ V$^{-1}$ s$^{-1}$ at 230 °C. Given the typically Arrhenius-like thermally activated character of the hopping process, it is typically the mobility (rather than the thickness of the oxide or the internal electric field) that determines the thermal stability of trapped charges and the corresponding surface potential.\(^2\)

Even the least stable electrets in this work (i.e., $d_{\text{ox}} = 0.3 \mu m$, and in this test $\sigma_{\text{in}} = -1.3$ mC m$^{-2}$) exhibit a characteristic decay time exceeding 15 min at 230 °C, which indicates a significant improve in stability compared to polymer electrets charged by corona discharge (see Section 3).

3. Discussion

The observations described above can be summarized in a simple picture of the energy landscape experience by a charge carrier, as sketched in Figure 6. In view of the homogeneity and electrical neutrality of water, the energy within the liquid is constant, except for the immediate vicinity of the polymer surface, where the electric double layer and other short range molecular forces give rise to an interfacial energy barrier ($\Phi_I$, see local potential maximum at the water–FP interface). Within the polymer, the charge carriers (which could be electrons or ions or both)\(^17,18,43–45\) experience a distribution of energetically more favorable locations (traps) separated by local energy barriers ($\Phi_I$). Amorphous fluoropolymers such as Teflon AF are known to be porous on the molecular scale (this is essential, e.g., for their application as gas filtration membranes), implying the presence of sub-nanometric voids separated by polymer material.\(^2\) This results in a distribution of traps with a characteristic depth that is related to the dielectric strength of the material. We schematically represent this situation by a sinusoidal energy landscape in the top panel of Figure 6 at zero voltage. Within the silicon oxide, the situation is similar, except that the barriers between adjacent traps ($\Phi_{\text{BD,ox}}$) are substantially higher, as evidenced by the much higher dielectric strength compared to the polymer.

As the charging voltage is applied, the energy landscape is tilted (see middle panel of Figure 6). As a result the effective barrier height “in the downhill direction” is reduced and charge carriers are injected into the material. From our experiments, we can infer several aspects about the hierarchy of the various energy barriers in the system: first of all, spontaneous charging of the surface is limited to surface potentials of the order of $U_0$, which is only a fraction of the typical surface potentials achieved at higher charging voltages. This indicates that there is a rather small density of trapped states at the polymer surface that is accessible by thermal energies. In fact, these states might be the ones that are populated spontaneously upon continued exposure of FP surfaces to water,\(^17,43–45\) and by the slide/triboelectrification process,\(^2,4,12,19,43–45\) The majority of charge carriers in our experiments, however, is only injected when the electric field exceeds the critical field $E_{\text{BD,ox}}$. The conclusion derived above that all injected charge carriers accumulate at the FP–oxide interface implies that the energy barriers within the polymer are much smaller than the “injection barrier” at the water–FP interface (i.e., $\Phi_I \ll \Phi_J$). Hence, we come to the conclusion that the “breakdown” of the FP layer is actually not governed by the intrinsic bulk properties of the material, but rather by the energy barrier to charge injection from the aeous phase. This—somewhat tentative—conclusion sheds new light on the origin of the much higher dielectric strength of $\approx 200$ MV m$^{-1}$ reported in EW experiments with thin films of Teflon AF (ref. \(^46\), and also reproduced here) compared to the lower values of around 20 MV m$^{-1}$ reported in the literature for bulk Teflon AF.\(^46,48,49\) According to our present findings, EW thus probes in the first place the injection barrier and not the bulk dielectric strength. Hence, we conclude that charge carrier injection limits the charging process. Somewhat intriguingly, the actual nature of the charge carriers—electronic or ionic—in our experiments is not clear. The same uncertainty applies to other corona- and triboelectrical charging experiments\(^17,18,20,43–45\) and also to the origin of the long debated negative surface charge of FP–water interfaces.\(^50,51–53\) While previous EW experiments demonstrated a clear dependence of the dielectric breakdown of thin FP films on the nature of ions,\(^50\) test extensions of the present measurements using purely electron-conducting liquid metals (data not shown) displayed similar charging behavior as the water-based experiments discussed above. Clearly, more dedicated experiments (e.g., as in ref. \(^45\)) is needed to identify the nature of the dominant charge carriers.
Notwithstanding these uncertainties, the effective charge densities reported here for Teflon AF–SiO2 composite electrets exceed by far most of the classical and recent slide/triboelectric nanogenerators (IENGs) and charge-excitation triboelectric nano-generators (CE-TENGs) as well as h-EWCI with Cytop FP. In particular, they also exceed reported values for corona-charged single layer Teflon AF electrets, for which the charge density is limited by the intrinsic breakdown strength of the material, in agreement with our conclusion that the SiO2 rather than the FP limits the maximum charge density. The maximum charge density reported for SiO2 is ~7.5 mC m\(^{-2}\), which is close to the highest values of the interlayer charge density of -5.1 mC m\(^{-2}\) inferred for some of our samples (see Figure S4 in the Supporting Information). Our model implies a clear roadmap toward further optimization of the parameters for maximum energy harvesting in nanogenerators—while respecting the intrinsic limitations of the materials involved (see Figures S5 and S6 in the Supporting Information).

Comparison to conventional FP-based electret materials also allows us to estimate the expected lifetime of our materials at room temperature. Widely used chemically similar Teflon FEP displays significantly higher values of the trap-modulated mobility at lower temperatures (e.g., 1.6 × 10\(^{-16}\) m\(^2\) V\(^{-1}\) s\(^{-1}\) at 145 °C, and 10\(^{-17}\) m\(^2\) V\(^{-1}\) s\(^{-1}\) at 185 °C). Spin-coated films of Teflon AF and other amorphous polymers as well as recently reported ultra-stable evaporated FP layers display a sharp decay of their surface potential within minutes upon exceeding the glass transition temperature (160 °C for Teflon AF 1600). Nevertheless, the systematic analysis of these materials suggested charge lifetimes of thousands of years at room temperature. Given the higher stability of our samples, the lifetime of the charge in h-EWCI charged composite electrets can be expected to exceed any commercially relevant product lifetime by far. Obviously, other failure modes such as fouling due to environmental conditions, or mechanical delamination or cracking due to applied stresses in a specific application may interfere at earlier stages.

While bare silicon oxide electrets allow to achieve even higher effective surface charges they do, however, suffer from bad resistance to humidity due to discharging via surface conductivity—a severe disadvantage for any application involving harsh environments that is shared by other recent charging methods proposed for nanogenerators. As our analysis shows, the composite oxide–FP thus harvest the benefits of both materials, the excellent dielectric strength and thermal stability of silicon oxide and the water repellence (or arbitrary salinity) by the protective FP coating. This combination is thus expected to enable high performance long term stable applications of composite electrets in harsh environment for nanogenerators but also for other electret applications that hitherto required encapsulation to suppress the detrimental effects of ambient humidity.

4. Conclusion

Composite electrets consisting of a stack of an inorganic oxide of high dielectric strength and a top coating of a fluropolymer in combination with the voltage controlled h-EWCI allow to generate surfaces with an extremely stable and high surface charge density. The superiority of these samples compared to other charging methods arises from the deep injection of charge carriers through the polymer to the oxide surface. Charge relaxation occurs only at temperatures substantially above the glass transition temperature of the polymer and is governed by thermally activated charge carrier transport across the oxide barrier. Charge relaxation due to ambient humidity or impacting water drops is suppressed by the FP layer that effectively isolates the trapped charge carriers at the FP–oxide interface from the effects of a potentially harsh environment. Our phenomenological model captures all relevant aspects of the experiments, including the critical voltages for charging and breakdown and provides perspectives how charge densities up to the limiting charge density of the bulk oxide material can be achieved.

5. Experimental Section

Sample Fabrication: Samples were prepared in a Class 100 Cleanroom (University of Twente), based on a p-type (100)-oriented silicon wafer, used as a bottom electrode. A silicon dioxide layer was thermally grown in a dry or wet environment (Table 1), cleaned in 99% HNO\(_3\) for 2 min, and rinsed afterward by purified water. The sample was coated with 300 nm, 1 μm, or 1.1 μm Teflon AF1600 (Chemours, 3% solution in FC-40 for 300 nm, and nondiluted for 1 and 1.1 μm) by spin-coating at 4000 RPM (300 nm) or 1500 RPM (1 and 1.1 μm). Hereafter, the samples were annealed on a hot plate (85 °C for 1 min and 185 °C for 1 h) and cut into ~2 cm by 3 cm pieces.

An external DC charging voltage \(U_c\) (generated by an Agilent 33220 function generator and amplified using a Trek PZD7000 amplifier) was applied for a set time (2 min to 4 h) between the grounded doped silicon bottom electrode and a large aqueous puddle, a \(1 \times 10^{-3} \text{ m} \text{NaOH} \) (Sigma-Aldrich) solution. \(U_c\) was with respect to the ground electrode. The area under the contact line was marked in polypropylene tape to apply a homogeneous electric field.

Measuring Surface Potential: The surface potential was measured by using the sample as a nanogenerator, such that the surface potential can be derived from the generated (peak) current. A droplet (33 μL, 0.1 m NaCl, conductivity: 4.85 mS cm\(^{-1}\)) was dropped next to a sample-mounted wire (platinum, \(d = 0.1 \text{ mm}\)) connected to the bottom electrode via a load resistor and a current amplifier (Zürich Instruments HF2TA, data acquisition by Tektronix TDS5034B Digital Phosphor Oscilloscope at 5 MHz). When the droplet touched the wire, counter charge that was initially in the bottom electrode was redistributed to the droplet as in a rapid discharge of the RC-circuit formed by the load resistor and the dielectric capacitance. The conductivity of the droplet was sufficiently high such that the droplet resistance can be neglected. The surface potential then is given by \(U_d = I_{\text{peak}} R_l\), where \(I_{\text{peak}}\) is the initial (peak) generated current \(R_l\) is the used load resistance. For each datapoint, nine current measurements were taken with three different oxidation conditions.

| Table 1. Silicon dioxide growth temperature, time, and, wet/dry oxidation. |
|---|---|---|---|
| \(d_m\) [μm] | Temperature [°C] | Time | Dry/wet oxidation |
| 0.03 | 1050 | 14 min | Dry |
| 0.30 | 1100 | 4 h 35 min | Dry |
| 2.0 | 1150 | 12 h | Wet |
| 3.6 | 1150 | 21 h | Wet |
load resistors (Figure 1f). For details, we refer to refs. [13,14]. Annealing of the samples to assess their thermal stability was performed in an oven. After annealing, samples were quickly cooled to room temperature, after which the surface potential was assessed by the drop-impact method discussed above.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
charge injection, droplets, electrets, electrowetting, nanogenerators

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