Microstructure and Corrosion Characterization of a MgO/Hydroxyapatite Bilayer Coating by Plasma Electrolytic Oxidation Coupled with Flame Spraying on a Mg Alloy

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ABSTRACT: Thermally sprayed hydroxyapatite coatings are one of the main strategies to improve the bioactivation of metal implants. However, the naturally low corrosion resistance of these coatings is the main challenge for their use. In this study, plasma electrolytic oxidation (PEO) was used to create an intermediate layer. The anodization process was used for comparison. According to the polarization curves, the PEO layer was more effective than the anodized layer in reducing the corrosion current density (I_corr of 0.05 × 10^−9 A/cm² vs I_corr of 0.05 A/cm²). The results of electrochemical impedance spectroscopy showed higher resistance of the sample with a PEO interlayer than that of the sample with an anodized interlayer. The results of the hydrogen evolution test revealed that the PEO layer as a middle layer served as the main barrier for reducing the magnesium corrosion rate, especially during the initial immersion time.

INTRODUCTION

Magnesium (Mg)-based alloys are materials of high demand because of their high strength-to-weight ratio.1 Their biodegradability and mechanical properties make them good candidates for implant applications. Mg-based alloys can be gradually absorbed in the body, and there is no need for a second surgery after implantation to remove them. However, the high corrosion rates of Mg alloys restrict their orthopedic applications.2 Recent studies have focused on controlling the high corrosion rates of Mg-based implants. For this purpose, various coating techniques have been used.3−7 Thermal spray is one of them. Thermal spray coating is a commercial method for the deposition of hydroxyapatite (HA) on metallic implants.8 Researchers have used various types of thermal spraying for HA coatings, such as plasma spraying, suspension plasma spraying, solution precursor plasma spraying, flame spraying, vacuum plasma spraying, and high-velocity oxygen fuel spraying.9−13 Simple control of the spraying parameters and the ability for large-scale production are the common benefits of these methods. However, the main drawback is the residual stress derived from the gradient of the thermal expansion coefficient between the HA coating and the metallic substrate during cooling. Utilizing an intermediate layer is suggested to overcome this problem. This layer should have the chemical composition and thermal expansion coefficient similar to those of the coating and the substrate.14,15

Yang used a porcelain intermediate layer between an HA coating and an alumina substrate. It was shown that the bond strength between the HA coating and the Al₂O₃ substrate could be improved.16 In another work, a TiO₂−HA bilayer on a Ti substrate was created, and the corrosion resistance and adhesion strength were enhanced. It was shown that with a decrease in residual stress, the number of cracks across the coating was reduced. By reducing the number of cracks, the penetration of the solution through the coating is reduced, resulting in increased corrosion resistance.17

Plasma electrolytic oxidation (PEO), also known as microarc oxidation (MAO), is a promising way to effectively improve the corrosion resistance and biocompatibility of metals used in valves (e.g., Al, Ti, Zr, and Mg alloys). Blawert et al. reviewed PEO, magnesium anodic oxidation, and MAO processes used for the surface protection of magnesium. An electrochemical
corrosion study of the performance of a pulsed constant current silicate-based PEO coating on pure Mg in a simulated body fluid (SBF) showed a higher corrosion resistance than that of the bare substrate.\textsuperscript{18} There are numerous studies on improving bioactivity with an HA coating as the top layer on a MgO surface. Gao et al. fabricated rodlike nanohydroxyapatite on a MAO coating via electrochemical deposition. They measured the bonding strength between the HA film and the MAO coating, revealing that it was almost 2 times higher than that of the coating applied via direct electrochemical deposition. The enhancement in the bonding strength and deposition improved the corrosion behavior.\textsuperscript{19} Shi et al. studied the MAO process of dicalcium phosphate dehydrate composite coatings on Mg alloys for degradable implant applications. The results revealed that the composite coating significantly reduced the corrosion rate of the Mg alloy and simultaneously enhanced the deposition of apatite on the coating.\textsuperscript{20}

In our previous studies, a MgO intermediate layer was used to reduce the HA coating corrosion rate on a Mg alloy.\textsuperscript{21,22} An anodizing treatment was used to produce the magnesium oxide layer. However, there are only limited studies in which PEO is applied to create an intermediate layer of MgO. PEO is a high-voltage process in which plasma discharges are created on the surface of a material. Partial fusion of the oxide layer leads to the adhesion of an oxide coating on the surface.\textsuperscript{23} In the present study, this method is compared to the anodizing treatment in terms of the ability to improve the corrosion resistance of magnesium alloys.

\section*{EXPERIMENTAL SECTION}

\subsection*{Preparing the Samples.} Specimens of an AZ61B-H24 magnesium alloy with a size of 15 mm × 15 mm × 5 mm were prepared. The chemical composition of the alloy was analyzed using X-ray fluorescence (Bruker, USA). The determined composition was Al 5.50%, Zn 1.5%, Mn 0.78%, and Si < 0.02%, and the remaining mass fraction was Mg. The specimens were ground using SiC papers (600–2000 grit). The samples were subsequently cleaned ultrasonically in acetone for 5 min, rinsed in distilled water for 5 min, and finally dried in warm air.

The PEO process was performed in an electrolyte containing 10 g/L Na$_3$PO$_4$ (99% purity, Merck) and 1 g/L KOH (98% purity, Merck). The magnesium alloy specimens were used as the anode, and two stainless steel plates were used as the cathode. A lab-produced pulse unit with a direct current (DC) power supply was employed to create the unipolar electric field. The PEO treatment was performed using a laboratory produced pulse unit with a constant current density of 2 mA/cm$^2$, a pulse width of 80%, an anodic voltage of 300 V, and a pulse frequency of 10 kHz. The samples were then placed in a furnace (Nabertherm, Germany) at 1200 °C for 2 h. A spray drying process (LabPlant SD-basic) was used to modify the morphology of the powders to become semispherical to increase their flowability during spraying. This process was carried out using distilled water solvent with a concentration of 0.5% mol/L with a heat output of 115 °C and a pressure of 5 bar. The flame spraying process parameters are given in Table 1.

\begin{table}[h]
\centering
\caption{Process Parameters of the Flame Spraying Process}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
acetylene & oxygen & spray distance & powder feeding rate & scan rate & spray gun \\
\hline
0.5 bar & 1.5 bar & 10 cm & 20 g/min & 0.5 m/s & GTV Unispray, Germany \\
\hline
\end{tabular}
\end{table}

\subsection*{Characterization.} After spray drying of the powders, their particle size distribution was characterized by dynamic light scattering (Horiba, LA931, Japan) with a 5 mV helium–neon laser and a $\lambda$ of 632.8 nm. For this purpose, distilled water was used to prepare powder suspensions. The morphology of the powder surfaces was studied using scanning electron microscopy (SEM) (Bruker, Germany) equipped with an energy-dispersive X-ray analyzer. An X-ray diffractometer (Bruker-Germany) was used to evaluate the phase compositions. Maud software was used to determine the weight percent of the phases from the X-ray diffraction spectrum. The phase quantitative analysis is performed using the following equation\textsuperscript{25}

$$I_{(hkl)\alpha} = \frac{K_{\alpha}K_{(hkl)\alpha}X_{\alpha}}{\rho_{\alpha} (\mu/\rho)_{\alpha}}$$

where $K_{\alpha}$ is an experimental constant that is different for each phase; $K_{(hkl)\alpha}$ is a phase constant, which is equal to the structural factor for the $\alpha$ phase; $X_{\alpha}$ is the mass fraction; $\rho_{\alpha}$ is the phase density; and $(\mu/\rho)_{\alpha}$ is the mass absorbance coefficient.

Corrosion tests were performed by electrochemical impedance spectroscopy (EIS) in SBF at 37 °C using a computer-controlled potentiostat system (ACM). The chemical composition of the SBF is shown in Table 2.\textsuperscript{26} A stirrer was used to homogenize the chemical composition of the electrolyte. A typical three-electrode system was used with the coated samples with a surface area of 0.5 cm$^2$ serving as the working electrode, a platinum wire serving as the counter electrode, and Ag/AgCl/sat KCl serving as the reference electrode. The frequency ranged from 0.1 Hz to 30 kHz, and the amplitude of the AC signal was ±10 mV. Equivalent circuits were designed using Z-view software. The corrosion tests were repeated three times. Potentiodynamic polarization tests employing an area of 0.25 cm$^2$ were performed at ambient temperature in the SBF solution, and a Ag/AgCl/sat KCl reference electrode was used. To perform this test, an AMETEK potentiostat (model PARSTAT 2273) was used. The volume of solution used in each corrosion test was 0.5 L.

For the hydrogen evolution test, a system similar to that used by Cui et al. was utilized.\textsuperscript{27} The corrosive solution was SBF, and the immersion time was 24 h. The volumes of hydrogen were recorded every 0.5 h.

\subsection*{RESULTS}

HA powder particles were produced from bovine bone by high-energy planetary milling and subsequent spray drying. A
detailed description of the powder production was given in our previous publication.22 The morphology of HA powders is illustrated in Figure 1a. The shape of the agglomerates is semispherical. The size of the agglomerated powders is between 18 and 155 μm (Figure 1b). The particle size distribution is given in Figure 1b. The size distribution is based on the volume of particles. The largest number of particles is in the region between 53 and 133 μm. The size of majority of particles is in the range of 67−133 μm. There is also a wide

PEO Coating Optimization. The microstructure of the PEO coating surface is presented in Figure 2. The mean pore sizes of the PEO coating produced at 400 and 450 V are approximately 4.5 and 5.6 μm, respectively. Moreover, interconnected pores are seen on the surface of the PEO coating at 450 V. This is due to the electrical spark and gas formation during the PEO process. The porosity percentage (calculated using ImageJ software using five images per sample) on the surface of the PEO coating created at 400 and 450 V is approximately 5 and 7.5%, respectively. Increasing the voltage causes larger electrical arcs during this process, which ultimately lead to the formation of pores on the surface. Basically, the pores on the surface are formed because of the two different types of discharges during this process. The first type is the discharge at the substrate−coating interface, which has a severe effect on the surface morphology. The other type is related to the gas discharge in the micropores, which creates smaller pores.28 The thicknesses of the PEO coatings produced at 400 and 450 V are approximately 9.6 and 12.5 μm, respectively. Another effect of using higher voltages is an increase in the layer thickness.

Table 2. Chemical Composition of the SBF Solution

| reagent       | NaCl | NaHCO₃ | KCl | K₂HPO₄·3H₂O | MgCl₂·6H₂O | CaCl₂ | Na₂SO₄ | Tris \(^{a}\) | 1.0 M-HCl |
|---------------|------|--------|-----|-------------|------------|-------|--------|-------------|-----------|
| g/mL          | 0.36 | 0.36   | 0.23| 0.23        | 0.31       | 0.29  | 0.07   | 6.11        | 0−5 mL    |

\(^{a}\)Tris-hydroxymethyl aminomethane.

Figure 1. (a) Morphology and (b) agglomerated powder size distribution of HA.

Figure 2. Microstructure of the (a) surface of PEO at 400 V, (b) surface of PEO at 450 V, (c) cross-sectional microstructure of PEO at 400 V, and (d) cross-sectional microstructure of PEO at 450 V.

Figure 3. Potentiodynamic polarization behavior of the PEO samples prepared at 300, 400, and 450 V.

Figure 4. SEM image of the (a) cross-sectional microstructure of PEO at 400 V, (b) cross-sectional microstructure of the anodized layer, (c) surface morphology of PEO at 450 V, and (d) surface morphology of the anodized surface.
The PEO process was carried out at three different voltages (300, 400, and 450 V). The sample treated at 450 V demonstrated the highest corrosion resistance in the potentiodynamic polarization test (Figure 3). The voltage values were chosen based on a previous work. In the sample treated at 450 V, the corrosion current density is less than the

Figure 5. SEM image of the (a) cross-sectional microstructure and elemental analysis of the PEO (at 450 V) + HA coating and (b) cross-sectional microstructure and elemental analysis of the anodized + HA coating.

Figure 6. SEM image surface morphology of the (a,b) PEO (at 450 V) + HA coating and (c,d) anodized + HA coating.

Figure 7. Elemental linear analysis of the cross-sectional microstructure of the (a) anodized + HA and (b) PEO + HA coatings.

Figure 8. X-ray diffraction patterns of the anodized layer, PEO coating, and Mg-based alloy.

Figure 9. X-ray diffraction patterns of the HA + PEO coating and anodized + HA coating.

The PEO process was carried out at three different voltages (300, 400, and 450 V). The sample treated at 450 V demonstrated the highest corrosion resistance in the potentiodynamic polarization test (Figure 3). The voltage values were chosen based on a previous work. In the sample treated at 450 V, the corrosion current density is less than the
others. However, the difference between the corrosion current densities for the samples treated at 300 and 400 V is not significant. The higher thickness of the coating produced at higher voltages caused less corrosion current in the sample. It seems that the effect of thickness is greater than the effect of porosity percentage. The difference in the porosity percentage is not significant. The corrosion potential is almost the same for all the three samples. Based on this characterization, the authors selected the PEO samples treated at 450 V and the anodized samples to compare their corrosion resistance.

Comparison of PEO and Anodized Coatings. The PEO coating produced at 450 V is considered for the following samples. The cross-sectional microstructure and surface morphology of the MgO layer of the PEO coating and the anodized coating are displayed in Figure 4. A porous coating is formed based on microdischarges during the PEO process. Pores with sizes between 1.5 and 7.8 μm are observed, and there are no cracks on the surface. The surface morphology and the cross-sectional microstructure of the anodized layer are shown in Figure 4b,d. The surface of this layer is porous with some cracks. The size of the pores on the surface is between 0.3 and 1 μm, and the thickness of the layer is in the range of 10–14 μm. The porosity percentage on the surface is approximately 6%. In comparison to the porosity of the coating subjected to traditional anodization, the porosity of the PEO coating increased. This is due to the higher voltage applied in the PEO process than in the anodization process.

Thermally Sprayed HA Coating. In Figure 5, the cross-sectional microstructure of the flame-sprayed HA coating on the PEO layer at 450 V is shown. The mean thickness of the HA layer is approximately 16 μm, and the oxide layer thickness is approximately 12.3 μm. The mean thickness of the HA layer in the anodized + HA coating is 11 μm and that for the MgO layer is approximately 2 μm. It is obvious that the reduced thickness of the MgO layer is due to the effect of blasting as a result of thermal spraying. This effect is not seen in the PEO + HA coating, which may be due to the stronger structure of the MgO layer formed in the PEO process than that of the layer formed by anodic oxidation. The roughness profile of the PEO + HA surface is higher and more irregular than that of the

### Table 3. Data Extracted from the Potentiodynamic Polarization Tests

| Sample          | $I_{\text{corr}}$ (A/cm²) | $E_{\text{corr}}$ (V) |
|-----------------|--------------------------|-----------------------|
| PEO             | $0.05 \times 10^{-7}$    | -1.5                  |
| PEO + HA        | $0.05 \times 10^{-9}$    | -1.5                  |
| Substrate       | 0.01                     | -1.5                  |
| Anodized        | 0.05                     | -1.25                 |
| Anodized + HA   | 0.05                     | -0.8                  |

Figure 10. Potentiodynamic polarization curves of the (a) anodized + HA coating, anodized coating, and substrate and (b) PEO and PEO + HA coatings in SBF solution.

Figure 11. Electrochemical impedance behavior: (a,b) Nyquist plots and (c,d) Bode plots of PEO and the PEO + HA coatings.
anodized + HA coating. Figure 6 shows the surface morphology of HA coatings. It is demonstrated that the flame-sprayed coating surface morphology is affected by the PEO surface morphology. Therefore, the surface of the HA coating is porous. The pore size is between 1.7 and 4.4 μm, and the porosity percentage is approximately 12.5%. In comparison with the porosity of the PEO layer, the porosity of the HA coating decreased from 13.1 to 12.5%, which may be due to the blocking of plasma discharge channels by the sprayed particles. By comparing Figure 6b,c, it is demonstrated that HA spots formed on the anodized surface are larger than those formed on the PEO surface. This can be due to the higher porosity on the PEO surface than on the HA surface. The roughness profile of the PEO + HA surface is higher and more irregular than that of the anodized + HA coating.

Figure 7 shows the linear elemental analysis of the HA coating on the anodized and PEO layers is shown. Magnesium is detected at three levels: near the surface, in the middle layer, and near the substrate. This result indicates the presence of two layers. The difference in the thickness of the MgO layer obtained by the PEO and anodizing processes can be seen. No new layer is formed between the HA layer and the PEO coating.

X-ray Diffraction Analysis. Figure 8 shows the X-ray diffraction patterns of the MgO layer produced on the Mg-based alloy substrate. This characterization confirms the formation of a magnesium oxide layer during the anodization and PEO processes. The Mg peaks are related to the substrate. The presence of the MgO phase is a result of the outward diffusion of Mg ions and the inward diffusion of OH⁻ at high potentials. The major reaction at the surface of the specimen results in oxide formation; the reactions are proposed as follows:

\[
\text{Mg} + \text{H}_2\text{O} - 2e^- \rightarrow \text{MgO} + 2\text{H}^+ \\
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- 
\]

The coating formation includes dielectric breakdown, sintering, and deposition processes. During the breakdown stage, melting and ejection occur. This causes the discharge channels inside the coating to remain as a conduit for the penetration of the melted materials to the surface. The ions and particles in the electrolyte can be compounded with the melted material to form new compounds. Discharges can generate the high-temperature areas where sintering occurs. High crystallinity and stable phases can be formed at highly intensive discharges.

Figure 9 shows the X-ray diffraction patterns of the HA coating on the PEO-coated and anodized substrates. The phase composition of this coating was MgO, HA, Mg, Ca₃(PO₄)₂, and Ca₄P₂O₁₉ phases. The maximum peaks are related to magnesium and magnesium oxide from the deeper layers. The X-ray diffraction pattern for the HA coating on the anodized substrate shows HA, Mg, tricalcium phosphate, and MgO phases. The HA + PEO coating has more intermediate phases and a lower content of the HA stable phase in comparison to those of the HA coating on the anodized surface.

Electrochemical Corrosion Tests. In Figure 10, the potentiodynamic polarization curves of PEO + HA and anodizing + HA coatings in the SBF solution are shown. According to Table 3, the I_corr value of the PEO + HA coating is much lower than that of the anodized + HA coating. The E_corr value of the PEO + HA coating is lower than that of the anodized + HA coating. Therefore, it can be concluded that the corrosion resistance of the PEO + HA coating is much higher than that of the anodized + HA coating. The E_corr values of the PEO coating and the PEO + HA coating are the same. However, the I_corr value of the PEO + HA coating is lower than that of the PEO coating. This implies that the corrosion
resistance is less improved by the HA layer than by the PEO layer. This improvement in corrosion resistance may be due to the reduction in surface porosity after thermal spraying.

Figure 11 shows the electrochemical impedance behavior of the anodized + HA coating and the substrate samples. The electrochemical impedance behavior of the PEO and PEO + HA coatings is shown in Figure 12. In both figures, the Nyquist plots consist of two loops. The first arc represents the outer layer properties and its pores with electrolytes, and the second arc represents the inner layer/metal interface. By comparing Figures 11a and 12a, it can be concluded that the effect of the PEO process on the improvement in corrosion resistance is much higher than the effect of the anodization process.

An equivalent circuit used to estimate the corrosion resistance values of single- and double-layer coatings is shown in Figure 13a,b. $R_s$ is the value of the solution resistance between the sample and the counter electrode. Figure 13a shows the equivalent circuit of single-layer coating. $R_{pore}$ and the fixed phase element $CPE_c$ are the resistances of the ion-conducting paths that develop in the coating and the capacitance of the coating, respectively. On the metal side of the pore, the coating delaminated and the electrolyte penetrated in it. This penetrated solution can be very different from the primary solution outside of the coating. The interface between the penetrated electrolyte and the substrate is modeled as a double-layer capacity in parallel with a kinetically controlled charge-transfer reaction. $R_{ct}$ and $CPE_{dl}$ correspond to the charge-transfer resistance and capacitance of this layer, respectively. In Figure 13b, the equivalent circuit used for fitting the double-layer coating is presented. $R_{pore}$ and the fixed phase element $CPE_c$ are the resistance of the ion-conducting paths that develop in the HA coating and capacitance of the HA coating, respectively. $R_f$ and the fixed phase element $CPE_f$ are the resistance and capacitance of the ion-conducting paths that develop in the MgO coating prepared by anodization or PEO, respectively.

| Sample            | $R_s$ (Ω cm$^2$) | $R_{pore}$ (Ω cm$^2$) | $R_{ct}$ (Ω cm$^2$) | $R_f$ (Ω cm$^2$) | $CPE_{dl}$ (F cm$^{-2}$) | $CPE_{ct}$ (F cm$^{-2}$) | $CPE_f$ (F cm$^{-2}$) |
|-------------------|------------------|----------------------|---------------------|------------------|--------------------------|--------------------------|---------------------|
| PEO + HA          | 1.06±0.03        | 0.79±0.02            | 3.18±0.05           | 0.69±0.03        | 0.74±0.06                | 0.84±0.05                | 0.85±0.03           |
| PEO               | 38.24±0.09       | 32.47±0.14           | 281.1±5             | 9406±3.5         | 0.76±0.05                | 0.87±0.06                | 0.84±0.05           |
| Anodized + HA     | 37.88±0.13       | 1413±1.6             | 9406±3.5            | 0.76±0.05        | 0.87±0.06                | 0.84±0.05                | 0.85±0.03           |
| Anodized          | 37.88±0.13       | 1413±1.6             | 9406±3.5            | 0.76±0.05        | 0.87±0.06                | 0.84±0.05                | 0.85±0.03           |
| Anodized + HA     | 38.24±0.09       | 32.47±0.14           | 281.1±5             | 9406±3.5         | 0.76±0.05                | 0.87±0.06                | 0.84±0.05           |
| Anodized          | 37.88±0.13       | 1413±1.6             | 9406±3.5            | 0.76±0.05        | 0.87±0.06                | 0.84±0.05                | 0.85±0.03           |

Figure 14. SEM image of the corroded surface of the HA + PEO coating.

Figure 15. Hydrogen evolution curves of the samples in SBF.
The results of the fitting of the EIS test data with this equivalent circuit using Z-view software are presented in Table 4. It can be seen that the corrosion resistance of the HA coating is also effective in terms of the corrosion resistance of the inner layer.

The surface microstructure of a coating can affect its corrosion resistance. The main characterization of the PEO layer is its porous structure. These pores can act as channels in the coating for the penetration of corrosive media. By depositing a thermally sprayed HA coating, these pores can be completely or partially filled.

The corrosion resistance of a coating depends not only on its microstructural properties but also on its chemical composition. In this case, the presence of a calcium phosphate layer on the surface facilitates the precipitation of calcium and phosphate ions on top of it. This can create an additional protective layer in the initial stages of corrosion.

The morphology of the corroded surface of the HA coating on the PEO layer is shown in Figure 14. Localized corrosion can be seen easily, and there are cracks in some areas. The deposition of calcium phosphate from SBF in the form of cauliflower particles on the surface is shown. Some cracks are filled by these precipitates. The energy-dispersive X-ray spectrum of the coating after corrosion for 12 h is shown in Figure 14. In comparison to that of the HA coating, the ratio of Ca/P increased from 1.7 to 2.7 in the corroded surface. This verifies the deposition of ions from the SBF on the surface. The presence of calcium phosphate precipitates on the surface can cause osteoconductive progression.

Hydrogen Evolution Tests. The results of the hydrogen evolution test in SBF at room temperature are presented in Figure 15. The amount of hydrogen gas released by the corrosion of Mg in the PEO + HA coating is less than that of the other samples. The hydrogen volume for the substrate is 20937–20947.

The authors would like to acknowledge the research support from Helmholtz Zentrum Geesthacht, Germany.

■ CONCLUSIONS
The effect of two coating processes for forming a MgO intermediate layer before applying a thermally sprayed HA coating on the corrosion behavior of a Mg-based substrate was investigated. PEO and anodization were used to form this MgO interlayer. The results revealed that in comparison to the anodization process, the PEO process can create a stronger coating in terms of corrosion resistance and impact resistance against the sprayed particles. The deposition of the subsequent layer (HA coating) on the PEO surface filled the pores and cracks on the surface generated by plasma discharges, which can increase the corrosion resistance because of the spatial separation between the surface and the solution. On the other hand, the presence of a calcium phosphate coating on the surface can facilitate the deposition of calcium and phosphate ions on it, thereby improving bone formation.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge the research support from Helmholtz Zentrum Geesthacht, Germany.

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