Comparison of Machine Learning Models on Performance of Single- and Dual-Type Electrochromic Devices

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ABSTRACT: This study shows that the model fitting based on machine learning (ML) from experimental data can successfully predict the electrochromic characteristics of single- and dual-type flexible electrochromic devices (ECDs) by using tungsten trioxide (WO3) and WO3/vanadium pentoxide (V2O5), respectively. Seven different regression methods were used for experimental observations, which belong to single and dual ECDs where 80% percent was used as training data and the remaining was taken as testing data. Among the seven different regression methods, K-nearest neighbor (KNN) achieves the best results with higher coefficient of determination (R²) score and lower root-mean-squared error (RMSE) for the bleaching state of ECDs. Furthermore, higher R² score and lower RMSE for the coloration state of ECDs were achieved with Gaussian process regressor. The robustness result of the ML modeling demonstrates the reliability of prediction outcomes. These results can be proposed as promising models for different energy-saving flexible electronic systems.

INTRODUCTION

Electrochromic (EC) applications encounter widespread accomplishment in smart windows for architectural buildings, (SageGlass, View, Inc.), autodimming rear view mirrors (Gentex), thermal control in space satellites, and infrared camouflage in military.1 EC smart windows are superiorly valuable for their aesthetic glazing to decrease glare and incoming solar irradiation into the buildings, decreasing the energy consumption of air conditioning in building by 26%, low energy consumption, and a good memory effect.2 However, the most of these EC technologies are generally generated on rigid substrates such as transparent electronics, adaptive camouflage, and biomimicry.3 In general, an ECD includes the transparent conducting electrode, the EC material, the electrolyte, the ion storage layer, and the counter conducting electrode.4 The traditional method of generating ECDs generally uses a “sandwich” configuration.4 The basic condition of an EC material is the reversible electrochemical oxidation and reduction behavior, with capability to sustain color change through intercalation or deintercalation of ions and injection or extraction of electrons with the exertion of voltage bias.5 The primary compounds with EC features are oxides of transition metals.5 The most widely used EC oxide is tungsten oxide (WO3) because of its advantages such as high contrast, high cyclic stability, and low material cost.5–7 The WO3-based EC film as a cathodically coloring material is changed from a bleached state (colorless) to a colored state (dark-blue).5,6,8 Especially, the secondary EC film (or so-called ion storage layer) is necessary for the ion storage layer for a complementary ECD.9,10 The role of using secondary EC film is to counterpoise the reaction in the main EC material and obstruct undesired reactions occurring on a nonfunctional counter electrode (generating chemical species that can degrade the functional potential).10 Vanadium pentoxide (V2O5) especially has attracted attention because of its unique features of anodic and cathodic coloration oxide, which can emerge the reversible optical parameter changes and multicolor changes during electrochemical reaction. Moreover, V2O5 is a typical Li+ intercalation compound, concerning its layered structure with good Li+ ions intercalation capacity that allows it to gain significant attention for battery and EC applications.10–12 However, V2O5-based ECDs have disadvantages including poor color contrast, when compared with some
EC materials (such as WO$_3$). Therefore, V$_2$O$_5$ films are usually utilized as just counter electrodes in ECD construction.

In the past, there were many studies based on modeling cathode-related phenomena in EC devices. For example, lithium ion transport behavior in diverse EC layers (such as WO$_x$NiO$_y$, etc.) was investigated using the finite diffusion model. Lusis et al. developed a model elucidating the dependence of coloration phenomenon on the constitution, the composition of the film, the atomic structure, and the size of tungsten oxide particles. A model was offered to explain the mechanism of the EC process in amorphous tungsten trioxide thin films. The proposed model showed that the kinetic was found to be controlled by the diffusion into the oxide of an intermediate species (M+, e$^-$). However, because of the complicated nature of the relation between the characteristics of ECDs, a precise mathematical model still remains unknown by now. One of simpler approaches is machine learning (ML), which is data-driven, that is, experimental data are necessary for the modeling. To the best of our knowledge, there is no report on a single- and dual-type flexible WO$_3$ ECD-based comparative research between experimental data and simulation using the ML model.

A branch of computer science that makes decisions on complex data and dedicates itself to build learning-capable algorithms is known as ML. Although research studies on chemical sciences have become more favorable in recent studies, ML and pattern recognition methods have long-standing background on chemical fields by including the linear learning method. Discovering new molecular targets and materials, giving insight into complexity of chemical data, modeling experimental structures, and overcoming possible chemical challenges are some of the enumerated applications of ML in chemistry.

In the literature, ML algorithms applied for various chemical studies especially in drug research, molecular structures, material science, and chemical patterns. Neural networks are trained to uncover unknown compounds that are pursued by a synthetic chemist. The reinforcement learning model is developed to design new molecules with specific desired properties with a partially automated framework, which is called Molecule Deep Q-Networks (MolDQNs). Melting point, pK$_{a}$, drug clearance, aquatic toxicity, and hERG blockade are the apparent properties of toxicological, pharmaceutical, and physicochemical, where the artificial neural network is used to make predictions. Moreover, random forest (RF) has been proven a very successful method in cheminformatics. Prediction of athletic performance enhancement, mutagenicity, hERG blockade, and skin sensitization are some of the studies where this approach is implemented. Support vector machines (SVMs) and kernel ridge regression preferred members of kernel methods. SVM is used to predict mutagenic toxicity, toxicity classification, and also hERG blockade. Besides these algorithms, K-nearest neighbors (KNNs) preserve their popularity with being simple and effective even though it is one of the first developed ML approach. This algorithm is mostly used in bioactivity studies especially in steroids anti-inflammatory, anticancer drugs, estrogen receptor agonists, and kinase inhibition.

Even though fields of ML are widespread, implementation of ML algorithms to ECDs is a rare subject. In one study, a model of adaptive neuro-fuzzy inference system (ANFIS) has developed to predict the good performance in the modeling of an EC device, especially in cases where noise is added to the input data. Dounis et al. introduced a novel approach for the modeling of an ECD. The proposed model using ANFIS showed a good performance in the modeling of a rigid ECD with the WO$_3$ film, especially in cases where noise was added to the input data. The ANFIS performance statistical indices mean absolute error, root mean square error (RMSE), and nondimensional error indexes were found to be near to zero. Values of coefficient of determination (R$^2$) and linear correlation coefficient ($\rho$) and variance account for are near to one.

The purpose of this study is to put forward a direct comparison between experimental data and ML algorithms for both the single- and the dual-type flexible ECDs. In accordance with this purpose, both tungsten trioxide (WO$_3$)- and WO$_x$/vanadium pentoxide (V$_2$O$_5$)-based flexible ECDs were fabricated as the single- and the dual-type flexible ECDs. To prepare the WO$_3$ film as the working electrode and the V$_2$O$_5$ film as the counter electrode, the radio frequency (rf, 13.56 MHz) magnetron sputtering method was selected because of its advantageous features such as having a good-quality film on large area substrates and a perfect adhesion between the film and substrates. Seven ML algorithms were used to generate models for the single- and the dual-type flexible ECDs where the charge density (mC/cm$^2$) is taken as the input, and the coloration of transmittance (%) and bleaching of transmittance (%) are predicted as the output. In this study, we have developed a simple, accurate, and fast ML model to predict EC performance for the single- and the dual-type flexible ECDs.

### RESULTS AND DISCUSSION

#### Material Characterization Results of the EC Electrodes

The morphology of the films of WO$_3$- and V$_2$O$_5$-coated onto indium tin oxide (ITO) films is shown in Figure 1a,c. The surfaces of the WO$_3$ and V$_2$O$_5$ films contain regular and the spherical grains with different sizes. As seen in Figure 1a, more agglomeration and bigger size of particles were obtained for WO$_3$ films because of thicker deposition onto ITO electrodes. The space between the grains has significant influence on movement of the ions and the electrons into the film that

![Figure 1. Scanning electron microscopy (SEM) images of (a) WO$_3$ and (c) V$_2$O$_5$ films and cross-section of (b) WO$_3$ and (d) V$_2$O$_5$ films.](https://dx.doi.org/10.1021/acsomega.0c03148)
allows it to improve EC performance such as switching time and coloration efficiency for EC applications. The thickness of WO3 and V2O5 films was measured as 489 and 269 nm, respectively (Figure 1b,d).

**EC Performance Using Experimental Assessment.**

Figure 2 shows the alternation of transmittance and charge density versus time because of the application of a potential step perturbation as well as the charge density response for all ECDs. The modulation range \( \Delta T \) \( (\Delta T = T_b - T_c) \), as shown in Figure 2a,c, is 57% and 67% for ECD-1 and ECD-2, respectively. The complementary ECD exhibited higher transmittance alternation than single-layer ECD. Clearly, an improved optical modulation (67% at 800 nm) was attained because of the simultaneous modulation of both EC electrodes. Li et al. fabricated a novel four-layered structure of glass/ITO/Li-NiO/Li-WO3/ITO/glass using e-beam and resistive heating evaporation technique. The fabricated ECD showed a good optical transmittance modulation (32%). In another study, Sydam et al. showed that ECD configuration was composed of the WO3−poly(butylviologen) (PBV) layer-by-layer film as the cathodic layer and ruthenium purple (RP) as the anodic layer. An outstanding transmission modulation of 49% was observed for the WO3−PBV/RP device. In this study, the obtained optical modulations for all ECDs were within the acceptable optical contrast range above 40% for both transmissive/reflective color-switching devices.

For ECD-1, the alternation of transmittance was because of the intercalation/deintercalation of small cations (Li+) into the WO3 film. The reversible influence in the case of tungsten oxide can be described as an electro-chemical reaction (1). For ECD-2, the applied voltage of 4 V means that WO3 is oxidized while V2O5 is reduced. Conversely, upon reversing applied voltage (−4 V), WO3 is reduced while V2O5 is oxidized, in accordance with the redox reactions as given below (1 and 2).

\[
\text{WO}_3 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{WO}_3
\]  

\[
\text{V}_2\text{O}_5 + x\text{Li} \leftrightarrow \text{Li}_x\text{V}_2\text{O}_5
\]

The coloration and bleaching times are examined by in situ transmittance response at 800 nm, as shown in Figure 2a,c. The response time is commonly characterized as the required period for 90% of the optical change between the two equilibrium states (i.e., colored and bleached states) at the certain wavelength. Parameters \( t_c \) and \( t_b \) imply the coloration and bleaching time, respectively. For ECD-1, the \( t_c \) and \( t_b \) are found to be 25.82 and 33.66 s, respectively, slower than those of ECD-2 (12.64 and 17.62 s). The fast coloration/bleaching kinetics may be ascribed to the large active surface of both WO3 and V2O5 films that allow it to facilitate the penetration of electrolyte into the EC films and reduce the ion diffusion path. Panagopoulou et al. studied the EC performance of the prepared V2O5 thin films grown using the rf-sputtering method as a function of two growth parameters, O2 content and substrate temperature. The fastest switching time is found to be for the case of O2 = 6% content, with coloration and bleaching times of 19.5 and 20.25 s, respectively. In another study, the WO3 film was prepared onto the ITO-coated glass sheet using the electrochemical deposition method. \( t_c \) and \( t_b \) were calculated as 21.4 and 18.5 s for WO3-based ECD, respectively.

Table 1 displays the obtained EC characteristics of all flexible ECDs using experimental data, with the equations given below 3–5.

\[
\Delta T = T_{\text{bleached}} - T_{\text{coloured}}
\]

| devices | \( \Delta T \) (%) | \( t_c \) (s) | \( t_b \) (s) | CE (cm²/C) |
|---------|-----------------|--------------|--------------|-----------|
| ECD-1   | 57              | 25.82        | 33.66        | 63.92     |
| ECD-2   | 67              | 12.64        | 17.62        | 76.10     |

Figure 2. (a) Transmittance (monitored at 800 nm) of ECD-1, (b) charge density change of ECD-1, (c) transmittance (monitored at 800 nm) of ECD-2 between applied voltages of +4 and −4 V with a time step of 120 s, and (d) charge density change of ECD-2 between applied voltages of +4 and −4 V with a time step of 120 s (\( \Delta T, t_c \) and \( t_b \) denote optical contrast, the coloration and bleaching time, respectively).
\[ \Delta \text{OD} = \log \frac{T_{\text{bleached}}}{T_{\text{colored}}} \]

\[ \text{CE} = \frac{\Delta \text{OD}}{Q} \]

where \( T_{\text{bleached}} \) (%) is the transmittance of the ECD in the bleached state, \( T_{\text{colored}} \) (%) is the transmittance of the ECD in the colored state, OD is optical density, CE is coloration efficiency, and \( Q \) is the intercalated charge per unit area. The CE values were calculated as 63.92 and 76.10 cm²/C for ECD-1 and ECD-2, respectively. The higher CE of ECD-2 can be ascribed to the existence of counter electrode (V₂O₅). ECD devices with high CE values can imply less energy to accomplish the same EC effect.\(^\text{47}\) Our previous study showed the coloration efficiency (53 cm²/C) of ECD with V₂O₅–PEDOT as the working electrode and MoO₃ as the counter electrode.\(^\text{12}\) In another work, Patil et al. prepared vanadium pentoxide (V₂O₅)-mixed tungsten trioxide (WO₃) thin films using the pulsed spray pyrolysis method. A maximum CE of \( \sim 49 \) cm² C⁻¹ was attained for the V₂O₅ film mixed with 15% WO₃.\(^\text{46}\)

Hyperparameter Tuning. Hyperparameters are the parameters that can be defined by users to achieve better prediction results and avoid the over-fitting problems as well. It is a trending topic for computational studies because there is not an adequate and complete approach for it.\(^\text{49}\) Therefore, only “a best”, not “the best”, hyperparameters can be found with some methods such as grid search, randomsearch, bayesian optimization, gradient-based optimization, and even heuristics. In the present work, grid search with parallel processing is applied to all regression methods. By the heuristics. In the present work, grid search with parallel processing is applied to all regression methods. By the application of grid search method, 5-fold cross-validation separation is performed for controlling the over-fitting problem. Separated 80% train-data is divided into five validation sets while setting hyperparameters. Finally, trained data with tuned hyperparameters are evaluated by already separated 20% test data.

In Figures 3 and 4, brighter colors demonstrate higher \( R^2 \) scores while dark ones indicate the lower. Optimized hyperparameters of KNN and Gaussian process regressor (GPR) algorithms for ECD-1 and ECD-2 data are assigned and given in the Table 2. Rest of the hyperparameter tuning heat maps is given in the Supporting Information from Figures S1–S24.

![Figure 3. (a) Heat map of ECD-1 bleaching hyperparameter testing and (b) heat map of ECD-2 bleaching hyperparameter testing.](Image)

![Figure 4. (a) Heat map of ECD-1 coloration hyperparameter testing and (b) heat map of ECD-2 coloration hyperparameter testing.](Image)

**Model Performance Comparison.** Charge density, bleaching transmittance, and coloration transmittance data are significant features in view of performance evaluation for EC applications. Alternations in transmittance, which is based on charge density under applied voltage bias, show significant influence on EC performance such as optical contrast and coloration efficiency. The benchmark data that are used for the comparison is the ECD-1 data and ECD-2 data, given in Tables 3 and 4, respectively. The ECD-1 and ECD-2 dataset consist of charge density (mC/cm²), bleaching transmittance (%), and coloration transmittance (%).

Different accuracy scores can be obtained by different ML methods based on its learning approach. These approaches depend on correlation between the features and output as well as the distribution of acquired dataset. Moreover, selected performance metrics take an important part as well as the ML model itself. Among the seven different regression methods, KNN outperforms all other algorithms for bleaching in both data sets. GPR, on the other hand, prevails for the coloration prediction.

According to Figure 5a–d, test samples of KNN and GPR almost overlap with the normalized data for bleaching and coloration, respectively, which leads to higher \( R^2 \) score and lower RMSE. Its proximity to the lines demonstrates that the predicted values from KNN and GPR methods are nearly equal to the actual values. As given in Table 5, KNN performs the best results with 0.9998 \( R^2 \) score and 0.0049 RMSE for ECD-1; 0.9997 \( R^2 \) score and 0.0053 RMSE for ECD-2 on bleaching. Furthermore, 0.9997 \( R^2 \) score and 0.0040 RMSE for ECD-1; 0.9997 \( R^2 \) score and 0.0046 RMSE for ECD-2 achieved with GPR for coloration. High \( R^2 \) scores on the test set in both ECD-1 and ECD-2 propose a prediction model of a good transmittance value, which has indeed developed. Present study surpasses with lower RMSE, which is shown in Table 5 compared to the study by Dounis et al.,\(^\text{17}\) which found average RMSE as 0.1532 for bleaching by applying ANFIS-genfis2b and 0.2032 for coloration by applying ANFIS-genfis1c. As a result, the achieved prediction performance of ECD-1 and ECD-2 in this study is very competitive.\(^\text{17}\)

Prediction performance of the models is observed more clearly in Figure 6, which includes all \( R^2 \) scores and RMSE values for each ECD dataset under bleaching and coloration.
Linear regression and support vector regressor unfortunately return the least precise and accurate results. Although it could be seen unfavorable, this information gives an insight into how the data are distributed. KNN and GPR are on the contrary; finalize the prediction with lesser RMSE and higher $R^2$ scores. In detail examination, better performance with KNN on bleaching and GPR on coloration could be realized. As a result, the proposed ML model was found to be a suitable prediction model for single- and dual-type flexible ECDs consisting of WO$_3$ and WO$_3$/V$_2$O$_5$, respectively.

Based on performance of the methods, the best fitting models KNN and GPR were used to predict ECD parameters such as $\Delta T$, $t_b$, $t_c$, and CE. The EC characteristics were calculated by using the predicted transmittance value from the ML method, and the results are given in Figure 7 and Table 6.

As seen from Figure 7, curves obtained by using predicted bleaching and coloring transmittance data are almost the same curves with experimental results for both ECD-1 and ECD-2. As seen in Table 6, the calculated performance parameters of ECDs are acceptable when compared with experimental parameters. In particular, optical contrast ($\Delta T$) and bleaching time ($t_b$) of ECD-1 and coloration time ($t_c$) of ECD-2 were obtained very close to experimental data. However, CE values attained small differences between experimental and theoretical results. For instance, although the predicted CE value of ECD-1 from the ML method can lead to an overestimation, the predicted CE value of ECD-2 from ML method can lead to an underestimation. This assumption might not be appropriate for the predicted coloration efficiency with high accuracy and it might clarify better fit with the larger matrix of experimental

| Algorithm       | ECD-1 bleaching | ECD-2 bleaching | Gaussian process regressor | ECD-1 coloration | ECD-2 coloration |
|-----------------|----------------|----------------|---------------------------|------------------|------------------|
| $K$-nearest neighbor | ball_tree      | ball_tree      | $\alpha$                 | $10^{-14}$        | $10^{-14}$        |
| n_neighbors      | 4              | 2              | normalize_y              | true             | false            |
| P                | 1              | 1              | optimizer                | $\text{Fmin}_1\_\text{bfgs}_b$ | $\text{Fmin}_1\_\text{bfgs}_b$ |
| weights          | Uniform        | distance       | kernel                    | none             | none             |
| metric           | Minkowski      | minkowski      |                           |                  |                  |
| leaf_size        | 30             | 30             |                           |                  |                  |

Table 3. Experimental Data for ECD-1

| charge density (mC/cm$^2$) | measurements values $T_b$ (%) (bleaching) | measurements values $T_c$ (%) (coloration) | charge density (mC/cm$^2$) | measurements values $T_b$ (%) (bleaching) | measurements values $T_c$ (%) (coloration) |
|----------------------------|-------------------------------------------|-------------------------------------------|----------------------------|-------------------------------------------|-------------------------------------------|
| 1                          | 4.14                                      | 59.681                                    | 34                         | 8.25                                      | 12.023                                    |
| 2                          | 4.495                                     | 50.046                                    | 35                         | 8.5                                       | 12.908                                    |
| 3                          | 4.417                                     | 51.223                                    | 36                         | 8.75                                      | 13.152                                    |
| 4                          | 4.417                                     | 48.456                                    | 37                         | 9                                         | 14.414                                    |
| 5                          | 4.639                                     | 46.751                                    | 38                         | 9.25                                      | 14.879                                    |
| 6                          | 4.86                                      | 44.194                                    | 39                         | 9.5                                       | 16.174                                    |
| 7                          | 4.915                                     | 42.312                                    | 40                         | 9.75                                      | 16.883                                    |
| 8                          | 4.794                                     | 39.869                                    | 41                         | 10                                        | 18.067                                    |
| 9                          | 5.004                                     | 37.673                                    | 42                         | 10.25                                     | 19.093                                    |
| 10                         | 5.214                                     | 36.643                                    | 43                         | 10.5                                      | 20.115                                    |
| 11                         | 5.203                                     | 34.828                                    | 44                         | 10.75                                     | 21.709                                    |
| 12                         | 5.292                                     | 31.972                                    | 45                         | 11                                        | 23.824                                    |
| 13                         | 5.347                                     | 30.732                                    | 46                         | 11.25                                     | 24.887                                    |
| 14                         | 5.878                                     | 28.938                                    | 47                         | 11.5                                      | 27.521                                    |
| 15                         | 6.067                                     | 27.665                                    | 48                         | 11.75                                     | 29.248                                    |
| 16                         | 6.233                                     | 25.861                                    | 49                         | 12                                        | 31.274                                    |
| 17                         | 6.532                                     | 25.543                                    | 50                         | 12.25                                     | 33.577                                    |
| 18                         | 6.498                                     | 23.071                                    | 51                         | 12.50                                     | 36.411                                    |
| 19                         | 6.509                                     | 21.632                                    | 52                         | 12.75                                     | 39.345                                    |
| 20                         | 6.797                                     | 20.237                                    | 53                         | 13                                        | 42.965                                    |
| 21                         | 7.318                                     | 19.141                                    | 54                         | 13.25                                     | 46.751                                    |
| 22                         | 7.528                                     | 18.001                                    | 55                         | 13.5                                      | 50.792                                    |
| 23                         | 7.716                                     | 17.447                                    | 56                         | 13.75                                     | 54.832                                    |
| 24                         | 7.694                                     | 16.894                                    | 57                         | 14                                        | 58.629                                    |
| 25                         | 8.635                                     | 16.263                                    | 58                         | 14.25                                     | 61.419                                    |
| 26                         | 8.358                                     | 15.787                                    | 59                         | 14.50                                     | 62.305                                    |
| 27                         | 8.613                                     | 15.322                                    | 60                         | 14.75                                     | 62.858                                    |
| 28                         | 9.399                                     | 14.702                                    | 61                         | 15                                        | 62.692                                    |
| 29                         | 9.653                                     | 14.303                                    | 62                         | 15.25                                     | 62.493                                    |
| 30                         | 10.262                                    | 14.314                                    | 63                         | 15.50                                     | 62.072                                    |
| 31                         | 10.572                                    | 13.329                                    | 64                         | 15.75                                     | 62.017                                    |
| 32                         | 10.96                                     | 12.798                                    | 65                         | 16                                        | 62.548                                    |
| 33                         | 11.799                                    | 12.609                                    |                            |                            |                            |
data. Future work should focus on improving prediction of the coloration efficiency and validate the model for a larger experimental data. In the previous published article, a methodology, based on camera vision, was shown to measure current distribution in influences in EC smart windows. This study demonstrates that although the simulations match the experimental data fairly well, the local kinetic model needs to be improved further. In addition, CE performance depends on the intrinsic redox ability of the EC material, the doping level, applied voltage, film deposition process, and electrolyte interactions.

## CONCLUSIONS

ML methods are found to be useful models for modeling of flexible ECDs under the coloration/bleaching states. In this work, a comparison of performance of single and double ECDs was carried out for seven different ML methods with hyperparameter tuning, which optimizes parameters of algorithm itself. Grid search with 5-fold cross-validation and parallel processing are applied to all regression methods to optimize the hyperparameters. Among different ML methods, KNN and GPR models have better estimation performance for flexible ECD-1 and ECD-2 under coloration and bleaching states, respectively. In addition, best prediction model’s robustness was also examined to demonstrate the reliability of prediction outcomes. One of the most significant ECD parameters for suitability to the real-life applications is the response time, which can be defined as the time required to switch between different EC states. Transmittance values with respect to response time are predicted, therefore, it would be beneficial to approximate peak points and ease the further experiments that are required, along with this study. Transmittance estimation with rapid and accurate algorithms has also a significant impact on flexible EC applications. Moreover, the EC characteristics like $\Delta T$, $I_r$, $I_b$, and CE were successfully calculated by using the predicted transmittance value from the experimental data. Future work should focus on improving prediction of the coloration efficiency and validate the model for a larger experimental data. In the previous published article, a methodology, based on camera vision, was shown to measure current distribution influences in EC smart windows. This study demonstrates that although the simulations match the experimental data fairly well, the local kinetic model needs to be improved further. In addition, CE performance depends on the intrinsic redox ability of the EC material, the doping level, applied voltage, film deposition process, and electrolyte interactions.

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Figure 5. (a) ECD-1 predicted bleaching transmittance, (b) ECD-1 predicted coloration transmittance, (c) ECD-2 predicted bleaching transmittance, and (d) ECD-2 predicted coloration transmittance vs charge density with 95% confidence interval.

Table 5. R² and RMSE Scores for Each Approach

|                  | DT       | RF       | KNN      | LR       | SVR      | GPR      | SGBR      |
|------------------|----------|----------|----------|----------|----------|----------|-----------|
| ECD1_Bleaching   |          |          |          |          |          |          |           |
| R²               | 0.99754  | 0.99981  | 0.99985  | 0.82211  | 0.97982  | 0.99863  | 0.99794   |
| RMSE             | 0.01971  | 0.00549  | 0.00494  | 0.16763  | 0.05646  | 0.01472  | 0.01805   |
| ECD1_Bleaching   |          |          |          |          |          |          |           |
| R²               | 0.99753  | 0.99964  | 0.99824  | 0.82211  | 0.96261  | 0.99468  | 0.99754   |
| RMSE             | 0.01974  | 0.00754  | 0.01667  | 0.16763  | 0.07685  | 0.02899  | 0.01971   |
| ECD1_Coloration  |          |          |          |          |          |          |           |
| R²               | 0.98877  | 0.99645  | 0.9954   | 0.84803  | 0.95697  | 0.99978  | 0.99564   |
| RMSE             | 0.02834  | 0.01594  | 0.00575  | 0.10423  | 0.05547  | 0.00400  | 0.01765   |
| ECD2_Bleaching   |          |          |          |          |          |          |           |
| R²               | 0.99539  | 0.99927  | 0.99658  | 0.84803  | 0.95628  | 0.99928  | 0.98886   |
| RMSE             | 0.02834  | 0.02242  | 0.01564  | 0.10423  | 0.05591  | 0.00717  | 0.02822   |
| ECD2_Bleaching   |          |          |          |          |          |          |           |
| R²               | 0.99530  | 0.99922  | 0.99979  | 0.90373  | 0.96756  | 0.99827  | 0.99568   |
| RMSE             | 0.02488  | 0.01022  | 0.00531  | 0.11247  | 0.06598  | 0.01524  | 0.02407   |
| ECD2_Coloration  |          |          |          |          |          |          |           |
| R²               | 0.99530  | 0.99820  | 0.99693  | 0.90454  | 0.95659  | 0.99600  | 0.99536   |
| RMSE             | 0.02510  | 0.01553  | 0.02031  | 0.11318  | 0.07633  | 0.02316  | 0.02496   |
| ECD2_Coloration  |          |          |          |          |          |          |           |
| R²               | 0.99939  | 0.99375  | 0.99095  | 0.69661  | 0.93820  | 0.99972  | 0.99143   |
| RMSE             | 0.02650  | 0.02148  | 0.02585  | 0.14971  | 0.06757  | 0.00456  | 0.02516   |
| ECD2_Coloration  |          |          |          |          |          |          |           |
| R²               | 0.98991  | 0.98868  | 0.95963  | 0.69661  | 0.88330  | 0.99957  | 0.98988   |
| RMSE             | 0.02730  | 0.02892  | 0.05461  | 0.14971  | 0.09285  | 0.00563  | 0.02735   |
ML method with KNN and GPR approaches. In particular, optical contrast, bleaching time of ECD-1, and coloration time of ECD-2 matched well with experimental and ML approaches. As a result, the proposed ML methods are shown to be promising candidates in view of estimation of EC performance for flexible EC applications and can be initial estimators for the

Figure 6. Charts of $R^2$ and RMSE scores for each approach: (a) ECD-1 bleaching, (b) ECD-1 coloration, (c) ECD-2 bleaching, and (d) ECD-2 coloration.

Figure 7. (a) Experimental and predicted transmittance (monitored at 800 nm) of ECD-1 and (b) experimental and predicted transmittance (monitored at 800 nm) of ECD-2 between applied voltages of +4 and −4 V with a time step of 120 s ($\Delta T$, $t_c$, and $t_b$ denote optical contrast of the coloration and bleaching time, respectively).
devices with different physical properties such as area, thickness, and material. In future study, the proposed data-driven models will have been pioneering in the field of optoelectronic applications including the other EC materials such as conducting polymers.

**EXPERIMENTAL METHODS**

**Materials.** WO₃ and V₂O₅ targets (0.25 thickness, 2 in. diameter) were purchased from China Leadmat Advanced Materials Co. Ltd. Poly(methylmethacrylate) (Alfa Aesar), propylene carbonate (Sigma-Aldrich), lithium perchlorate (LiClO₄, Sigma-Aldrich), and acetonitrile (Merck) were used for gel electrolyte preparation for ECD. 10,52 ITO-coated polyethylene terephthalate (PET) substrates having a sheet resistance of 80–100 Ω/sq and 25 μm thickness were supplied from Teknoma Company/Turkey, and the cleaning solvent (ethanol) was applied to them prior to use.

**Experimental Details.** An electroactive WO₃ layer was deposited onto the ITO-coated PET substrate using the rf (13.56 MHz) magnetron sputtering method and used as the working electrode. Prior to deposition, the background pressure was set to 0.01 Pa. The WO₃ target was sputter-cleaned in an argon atmosphere for 10 min to eliminate surface contaminations. The working pressure and magnetron power were maintained constant at 1 Pa and 90 W with an Ar gas atmosphere, respectively. The distance between the substrate and target was 8 cm.

The V₂O₅ thin film was prepared onto the ITO-coated PET substrate under an Ar gas atmosphere using the rf magnetron sputtering method and served as the counter electrode. The deposition parameters were the background pressure of 0.01 Pa, working pressure of 1 Pa, and rf power of 140 W. The thickness of WO₃ and V₂O₅ layers onto conductive PET was controlled using an INFICON SQM-160 model thin-film deposition monitor during rf magnetron sputtering deposition.

The flexible ECDs were produced by sandwiching of the gel electrolyte between the working electrode (WO₃ film) and counter electrode (ITO film or V₂O₅ film for single- or dual-type ECs). The gel electrolyte was prepared like the mentioned preparation detail in our previous EC studies.10,52 Two ECDs were designed in following forms. Active area of ECD was 2.5 cm x 2.5 cm. The fabrication and performance measurements of ECDs were carried out at room temperature under proper conditions.

**Material Characterization.** The Gamry PC14/300 model potentiostat was used for EC characteristic measurements. Optical transmittance spectra were recorded using a computer-controlled setup of HR4000 (Ocean Optics, Dunedin, FL, USA) spectrophotometer. SEM—energy-dispersive X-ray spectroscopy (FEI Quanta FEG 250) was utilized to evaluate the surface morphology, cross-sectional images, and composition analysis of the prepared films.

**Prediction Models.** This study conducts seven different prediction approaches. Linear regression, the simplest model, is used to make comparison between different ML models. It is a linear approach that tries to estimate dependent variable over independent variables with fitting a linear line, and its working mechanism is based on minimizing the residuals. The K-nearest neighbor method is widely used for both classification and regression: in classification, the k-nearest points is taken into account for prediction while in regression, it is determined by average of k-nearest points.53 Decision trees, which branch of the tree presents a possible outcome or reaction, are constructed to demonstrate why the criteria are selected with mutually exclusive branches.54 One of the ensemble learning models, which is a random forest, combines multiple decision trees into one model to have an enhanced prediction result. Support vector regressors, which tries to fit the error in a specific threshold, use a hyperplane for prediction. Hyperplane that covers maximum points gives the best prediction results. GPR considers all possible functions to train the model. In contrast to traditional regressors, Gaussian regressor trains on the hyperparameters yet suffer from operational speeds. Stochastic gradient boosting outperforms gradient boosting with increased ensemble diversity because it adds further variance by splitting features and samples without replacement where gradient boosting may lead same split points and features. All these models have default internal variables or hyperparameters and whatever the model is they should be estimated optimally with methods like systematic and random searches or heuristics to have better performance.53 In this study, experimental data are collected from two types of ECDs, and charge density is set as the input variable while coloration and bleaching are used for predicted outputs. The total data (80%) and the remaining 20% part is used as training and testing for each ML algorithm, respectively. Additionally, in order to have a similar distribution to the initial data, stratify attribute is taken as equal to y (transmittance values). Therefore, both train (80%) and test data (20%) sets were distributed similar to the initial data set. When 20% test-data are separated for a final evaluation, 80% train-data set was used for 5-fold cross validation during the ML applications. After preprocessing the data, hyperparameters are tuned for the seven different ML methods that are briefly mentioned in the above and prediction performances for each algorithm, with and without hyperparameter tuning, are compared.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03048.

Further information for the heat maps of ECD-1 and ECD-2 (PDF)

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Electrochromic Tungsten/Iron Mixed Oxide Films Synthesized by WO3 Thin Films onto Flexible Polyethylene Terephthalate Substrates. Electrochromic Characteristics of Radio Frequency Plasma Sputtered Using Polymer Plasma Hybridization Process. Li-Doped Ion Gel Electrolytes for Flexible WO3-Based Electroceram. Int. Flexible Electrochromic Devices.

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03048

Author Contributions
E.C.G., M.O.Y., E.E., and A.U.O. participated in the design of this study and analyzed the data and wrote the paper. All the authors read and approved the final manuscript.

Notes
The authors declare no competing financial interest.

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