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Letter

Design of a Novel Voltage Controller for Conversion of Carbon Dioxide into Clean Fuels Using the Integration of a Vanadium Redox Battery with Solar Energy

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Abstract: This letter presents a design for a novel voltage controller (NVC) which can exhibit three different reactions using the integration of a vanadium redox battery (VRB) with solar energy, and uses only electrochemical potentials with optimal external bias voltage control to carry out hydrogen production and the conversion of carbon dioxide (CO_2) into methane and methanol. This NVC is simply constructed by using dynamic switch and control strategies with a time-variant control system. In this design, the interval voltage bias solutions obtained by the proposed NVC exhibit better voltage ranges and good agreement with the practical scenarios, which will bring significant benefits to operation for continuous reduction of CO_2 into value-added clean fuels using the integration of a VRB with solar energy or any other renewable energy resource for future applications.

Keywords: novel voltage controller (NVC); vanadium redox battery (VRB); solar; reduction of CO_2

1. Introduction

Renewable energy generation increase and carbon dioxide (CO_2) reduction targets have been included in energy policy in Taiwan. However, the growth of renewable energy brings new technical challenges to power supply. For instance, the inherent intermittency of photovoltaic (PV) power has given rise to a number of approaches to compensate for the variability in its output. As an effective technique for enhancing integration of intermittent renewable energy into a power supply, battery energy storage systems (BESSs) have become one of the focal points of development. A vanadium redox battery (VRB) is a type of battery with the potential to increase the supply reliability of PV power generation. VRBs are well suited for renewable energy applications. They have many attributes which make them an excellent choice for renewable energy applications [1,2].

The conversion of carbon dioxide into synthetic fuels (methane, methanol, etc.) recently using solar/BESS energy has obtained a great deal of attention from the scientific research community as it can deal with the energy crisis, global warming, and energy storage problems [3–5]. There are numerous routes for converting CO_2 to clean fuels, such as electrochemical (EC), photoelectrochemical (PEC), etc. [6]. In integrated PV and EC, sunlight is first converted to electricity by a photovoltaic cell and CO_2 is then reduced electrochemically [7], which shows outstanding potential for the CO_2 catalytic hydrogenation route [5]. In photoelectrochemical (PEC) routes, photogenerated electrons are used to convert CO_2 into synthetic fuels either directly at certain non-oxide semiconducting photoelectrodes or indirectly using a redox mediator [8]. These routes have been inadequate for performing on a commercial scale. This is due to the fact that these routes still need a certain amount of external bias voltage from the grid current. The reduction reaction of CO_2 is accompanied with water (H_2O) reduction. Hence, hydrogen (H_2) is a major byproduct which always competes with the CO_2 reduction reaction.

In general, a voltage control for bias potential is required to drive the H_2O oxidation in both PEC and EC route conversion of CO_2 into synthetic fuels in aqueous electrolytes [9–11]. Therefore, in this letter, we present a simple design for a novel voltage controller (NVC) using a standalone solar/BESS energy system to switch three different loop reactions in order to drive the reaction to carry out hydrogen production and the conversion of carbon dioxide into methane and methanol. The innovative contribution of this letter is the proposal of an NVC for dynamic optimal voltage bias control strategies, as well as a performance comparison of this work, indicating that this design concept is competitive.

2. Design of the Novel Control System for Conversion of Carbon Dioxide

Figure 1 shows the structure of the proposed novel voltage control for conversion of carbon dioxide into clean fuel using PV/VRB power generation. This novel control system mainly consists of the photovoltaic (PV) modules, a vanadium redox flow battery (VRB) as the energy storage, and a novel voltage controller which can provide the optimal external bias voltage to run the hydrolysis and conversion of carbon dioxide into methane and methanol.

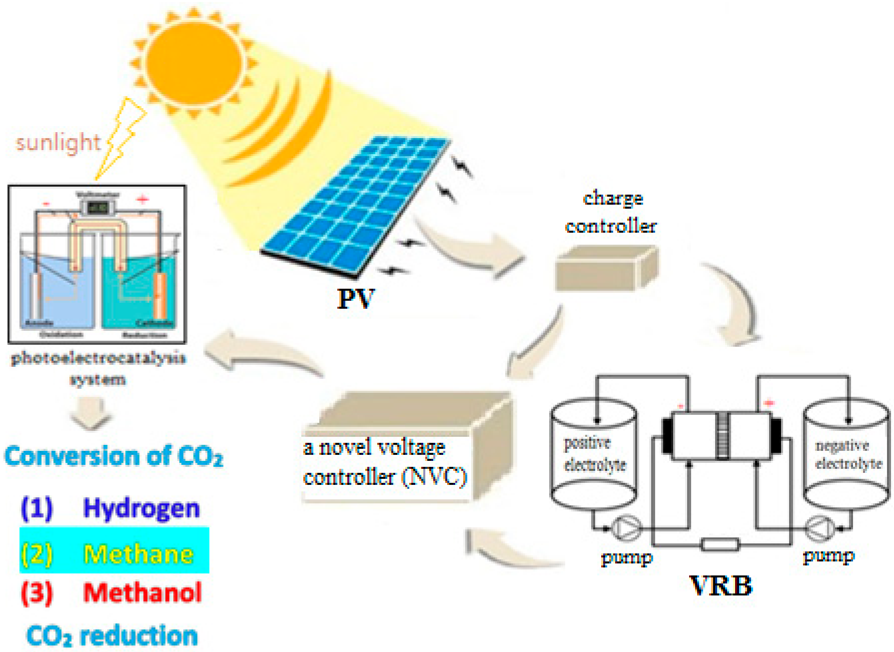


Figure 1. The structure of the novel voltage control for conversion of carbon dioxide into clean fuel using Solar/BESS (battery energy storage system) energy.

2.1. Integration of Vanadium Redox Battery with PV System

Figure 2 shows the detailed and proposed empirical electrical circuits for the PV system including the VRB [12]. The detailed model captures the electrical behavior of the standalone VRB under ideal environmental conditions [12,13].

A PV cell is a p–n junction, with characteristics similar to diodes, and the *I–V* and *P–V* characteristic curves of the PV array are nonlinear in nature. As a function, this nonlinearity is defined in terms of the voltage and current of the PV array as follows [14]:

$$I_{PV} = I_{SC} - I_{PVO}\left[exp\left(\frac{q(V_{PV} + I_{PV}R_s)}{nKT}\right) - 1\right] - \frac{V_{PV} + R_s I_{SC}}{R_{sh}}. \quad (1)$$

The VRB is a galvanic cell that uses ions dissolved, usually in an acidic solvent, as electrolytes. Thus, the energy is stored in fluids. The battery reactions which change the valence of the vanadium occur in both the positive and negative electrodes. The carbon felts act as porous electrodes for electrochemical reactions of vanadium ions at the two sides.

Positive electrode:
$VO^{2+} + H_2O \leftrightarrows VO_2^{+} + 2H^{+} + e^{-}$
Negative electrode:
$V^{3+} + e^{-} \leftrightarrows V^{2+}$
($\rightarrow$: charge, $\leftarrow$: discharge)

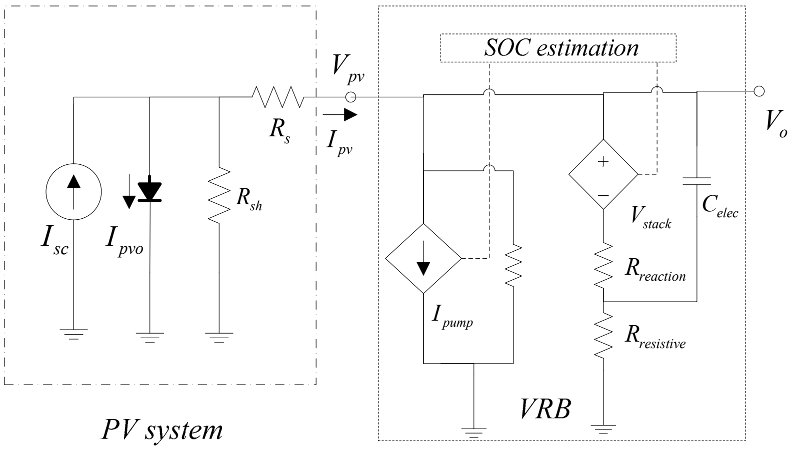


Figure 2. The electrical circuits for the integration of a vanadium redox battery (VRB) with a photovoltaic (PV) system. SOC: state of charge.

The electrochemical models of the VRB are based on the conservation law of mass, species concentration, and energy. Several VRB models have been developed [15–17]. These models give insights on membrane investigation, electrode design, electrolyte selection, and flow frame optimization [15,16].

The SOC (state of charge) which defines vanadium ion concentrations varies with time. The value is an indication of the energy level of the VRB, which is related to the concentrations of the different vanadium species. Generally, the state of charge can be calculated as follows [18,19]:

$$SOC = SOC_0 + \Delta SOC, \tag{2}$$

$$\Delta SOC = \int_0^t \frac{V_{stack}(t) \cdot I_{stack}(t)}{P_{rating} \cdot T_{rating}} dt. \tag{3}$$

The charging/discharge efficiency of the VRB is a function of load and SOC [17,19]. According to this simplified equivalent estimation of SOC under charging and discharging, the PV system including the VRB was modeled and the control parameters of the integration of the VRB with the PV system were reasonably designed to stabilize the fluctuations in power generation output [20–22].

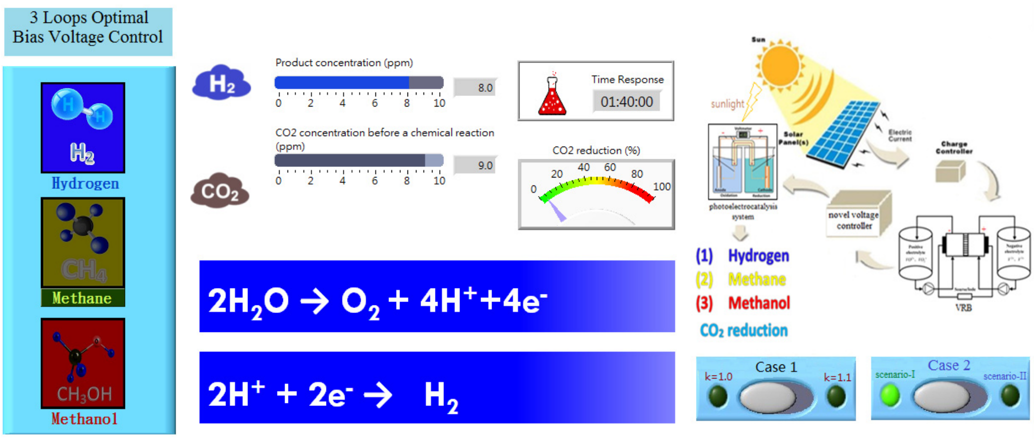
The power supply system is required to follow the supply/demand balancing rule. During the day, the PV system supplies the load and any excess energy is used to charge the VRB. During the night, the VRB supplies the load. When the VRB power is negative, this indicates that the VRB is absorbing power (charging). Therefore, the power can be calculated as follows:

$$P_{PV} \pm P_{VRB} = P_{Load}. \tag{4}$$

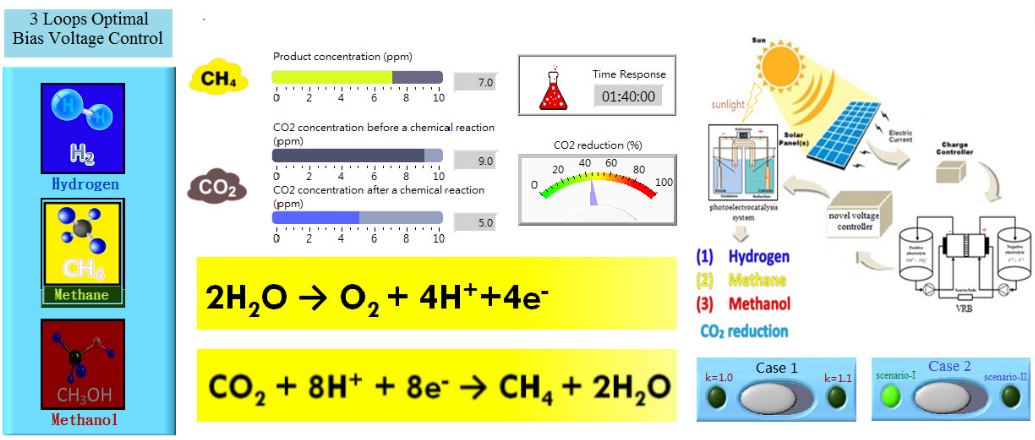
The integration of the VRB with the PV system is connected through circuit breakers to a dc bus. The system serves various loads, including pumps and heating elements, to emulate actual operational load behavior. A novel voltage controller is connected to the dc bus via a dc/dc converter.

2.2. Design of a Novel Voltage Controller

The conversion of carbon dioxide into synthetic fuels using solar/storage energy has received a significant quantity of consideration from the scientific community due to its potential to mitigate climate change and global warming [23,24]. An advance in the electrochemical reduction of CO_2 to hydrocarbons with high rates and efficiencies was seen in [25]; the evaluation recommends that verified technologies and sound, tested principles are made available to develop an integrated energy system relying on clean fuels [26]. Therefore, we design a novel voltage controller to switch the three-loop optimal bias voltage to run the hydrogen production and conversion of carbon dioxide into methane and methanol. Figure 3 shows a picture of the proposed three-loop optimal bias voltage control. The first loop is employed for hydrogen production from water. The second and third loops provide the different bias voltages to regulate the optimal production capacity for the conversion of carbon dioxide into methane and methanol, respectively. The three loops use solar/BESS energy exclusively, and are marked by design in blue (hydrogen), yellow (methane), and red (methanol).

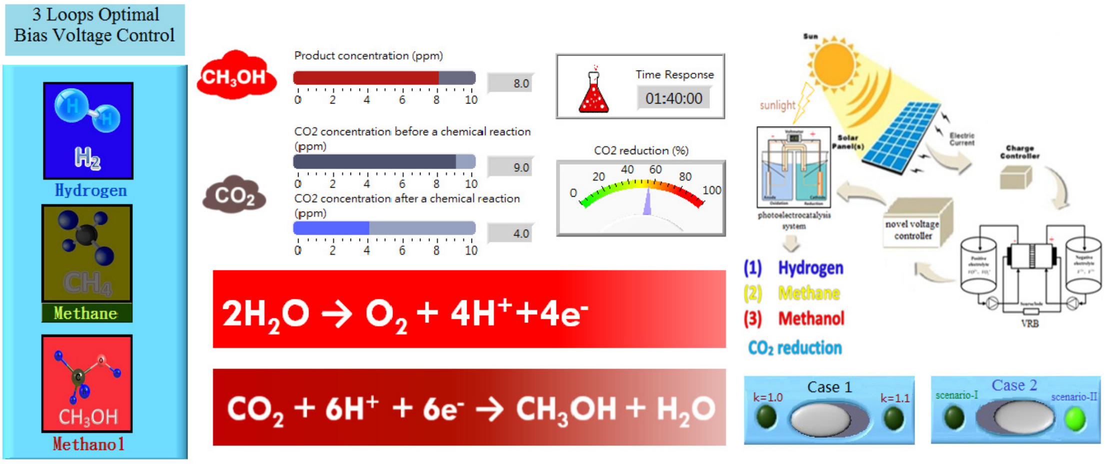


(**a**)



(**b**)

Figure 3. *Cont.*



(**c**)

Figure 3. (**a**) Hydrogen production from water (blue), (**b**) the conversion of carbon dioxide into methane (yellow), and (**c**) the conversion of carbon dioxide into methanol (red).

3. Proposed Optimal External Bias Voltage Control Method

Recently, the pathways and potential products of different CO_2 conversion routes depending on voltage control have been reviewed in many articles [9–11,27]. The photo and electrochemical reduction of CO_2 to hydrocarbons has been studied and several kinds of excellent catalysts have been developed [28]. One obvious advantage for the PEC and EC route is that it can produce a variety of products like hydrogen, methane, methanol, ethanol, propanol, and formic acid, depending on voltage control, and environmentally friendly products like water and oxygen [9,29,30]. The protons and electrons are generated from water which is oxidized at the anode by releasing electrons to reduce CO_2 at the cathode to various synthetic fuels such as methane, methanol, etc. In an aqueous electrolyte, CO_2 reduction is accompanied with H_2O reduction; hence, H_2 is a major byproduct, releasing carbon dioxide and combining the hydrogen back with oxygen to form water [29]. The formation of synthetic fuels is a combination of the reduction reaction at the cathode and the oxidation reaction at the anode [9,30].

Anode reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Cathode reaction:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \text{ or}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

3.1. Design of a Novel Three-Loop Voltage Controller

The electrochemical reduction of CO_2 requires electrical energy, with overpotential always >1 V (vs. standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE)) to get reasonable amounts of fuels [26,30]. A concept of an integrated energy carrier includes electricity plus hydrogen and synthetic carbon-based fuels. Therefore, we design a novel voltage controller (NVC) to switch three different loop reactions, and use only electrochemical potentials to drive the reaction to run the hydrogen production (Loop-01: V01-*k1*V01 vs NHE) and conversion of carbon dioxide into methane (Loop-02: V02-*k2*V02 vs NHE) and methanol (Loop-03: V03-*k3*V03 vs NHE), as shown in Figure 4. It facilitates the combination of the different potentials.

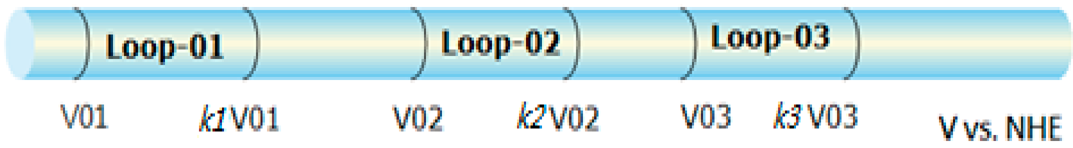


Figure 4. Three different voltage loops of the electrochemical reactions for the novel voltage controller (NVC). NHE: normal hydrogen electrode.

Figure 5 shows the detailed and empirical electrical circuits for the proposed system. Herein, R_0 is utilized as the variable resistor for the test cases to find the optimal voltage range and energy consumption. This would involve adjusting the electrode current density through changing the output voltage and current to capture the electrical behavior of the proposed three loop tests [31]. The energy consumption in a single-unit photoelectrocatalysis system [32] can be expressed as

$$E = \int_0^{t_n} (V_o - I_0^{(n)} R_0^{(n)}) \cdot I_0^{(n)} dt \tag{5}$$

where E represents the energy consumption in a single-unit photoelectrocatalysis system and n stands for the change times via adjustment of R_0 during total reaction time t_n.

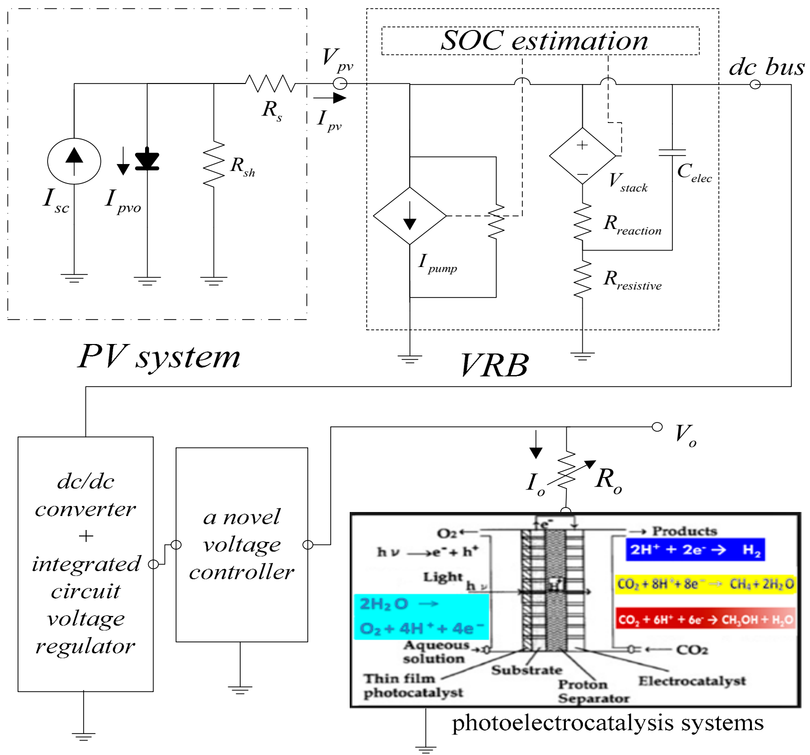


Figure 5. The empirical electrical circuits of the proposed system.

The major contribution of this letter is the proposal of an NVC using a standalone solar/BESS energy system for three-loop optimal bias voltage control for the production of hydrogen (Loop-01), methane (Loop-02), and methanol (Loop-03). This NVC can be programed by the designer for the control strategies through an Arduino module, which also allows working wireless control for the three loops' dynamic voltage outputs. Figure 6 shows the PCB (printed circuit board) layout of the NVC consisting of an Arduino module, adjustable positive linear voltage regulators (LM317), rheostats

(VR, SVR), diodes, filter capacitors, Loops 1–3 outputs and meters, etc. The parameters used in the proposed NVC are shown in the Appendix A.

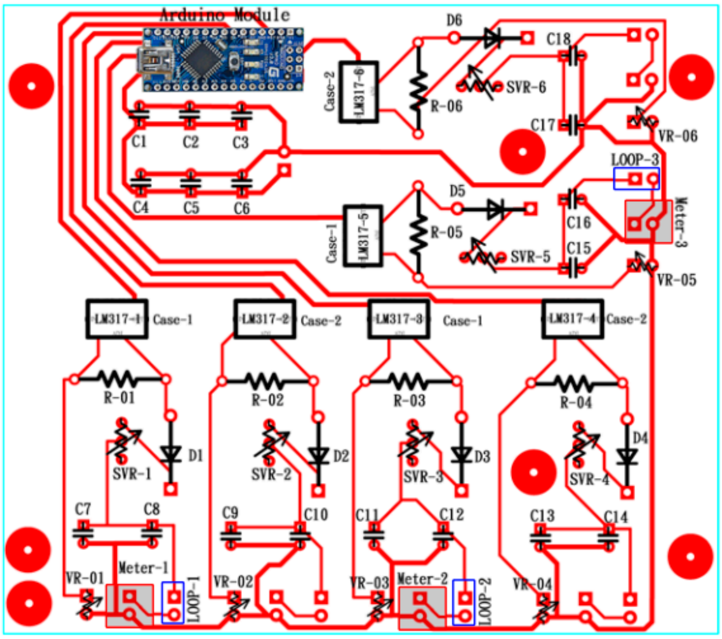


Figure 6. The printed circuit board (PCB) layout of the proposed NVC.

3.2. *Optimization Technique*

In this letter, the objective of connection adjustment of an NVC is traditionally to improve the invariant bias voltage control by minimizing the energy consumption and maximizing the CO_2 reduction while satisfying equality and inequality constraints of the electrochemical reactions. Therefore, the objective function of this study for the performance can be formulated as follows:

$$Minimize\ \mathrm{F}_i = \frac{E_i}{X_i} \quad i = 1,2,3 \tag{6}$$

where E_i represents the energy consumption that uses electric energy to induce production of hydrogen (i = 1), methane (i = 2), and methanol (i = 3). X_i is the actual production volume during the reaction time.

4. Case Studies

The cases are described here to illustrate the proposed optimal method under three different operating conditions. In this letter, in order to demonstrate the effectiveness of the proposed optimal external bias voltage control method, the following cases are examined.

Case 1: As shown in Figure 4, invariant bias voltage control is assumed (k = 1.0 and 1.2).

Case 2: In this case, two scenarios are considered for a simple time-variant system control. Thus, the external bias voltage would involve adjusting the variant k with fixed time intervals and changing the output voltage and current via the NVC. Two adopted step-by-step control methods in scenario-I (k = 1.0~1.2, n = 2) and scenario-II (k = 1.02~1.2, n = 10) and shown in Figures 7 and 8, respectively.

Many tests were carried out to test the NVC three-loop control for hydrogen (Loop-01), methane (Loop-02), and methanol (Loop-03) with the integration of the VRB with the PV system in various response times. Table 1 shows the given various reaction times for Case 1 and Case 2, where F is normalization by scaling between 0 and 1 by Equation (6), as well as a performance comparison of this work, indicating that this design concept is competitive.

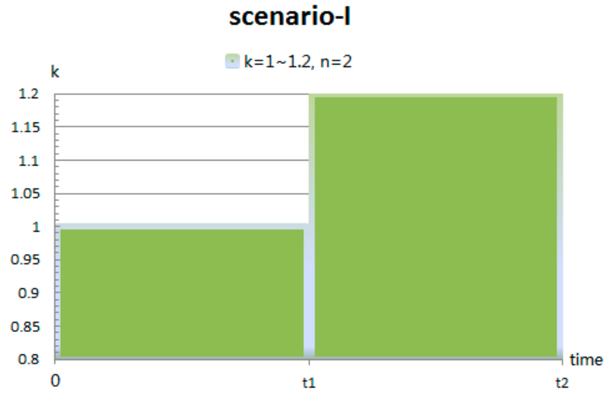


Figure 7. A simple time-variant control of the proposed NVC (n = 2).

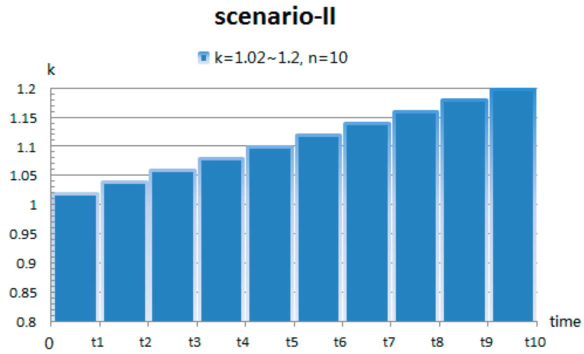


Figure 8. A step-by-step control with fixed time intervals for the proposed NVC (n = 10).

Table 1. Performance comparison of the cases at various reaction times.

$\mathbf{F}_i = \frac{E_i}{X_i}$	**Case 1**		**Case 2**	
	***k* = 1.0**	***k* = 1.2**	**Scenario-I**	**Scenario-II**
Hydrogen	$F_{1,\,1\text{-}1}$	$F_{1,\,1\text{-}2}$	$F_{1,\,2\text{-}1}$	$F_{1,\,2\text{-}2}$
Methane	$F_{2,\,1\text{-}1}$	$F_{2,\,1\text{-}2}$	$F_{2,\,2\text{-}1}$	$F_{2,\,2\text{-}2}$
Methanol	$F_{3,\,1\text{-}1}$	$F_{3,\,1\text{-}2}$	$F_{3,\,2\text{-}1}$	$F_{3,\,2\text{-}2}$

5. Conclusions

In this letter, the integration of a VRB with a PV power generation system was proposed and implemented on microgrid. This standalone PV/VRB generation system can effectively extract the maximum power from solar energy to provide the optimal external bias voltage via a dc/dc converter and the proposed NVC to carry out hydrogen production and the conversion of carbon dioxide into synthetic fuels. From the case studies, we can see that the optimal external bias voltage and energy can be well controlled under three different loop reactions, and use only electrochemical potentials to drive the reaction to run the hydrogen production (Loop-01: V01-*k1*V01 vs. NHE) and conversion of carbon dioxide into methane (Loop-02: V02-*k2*V02 vs. NHE) and methanol (Loop-03: V03-*k3*V03 vs. NHE).

Renewable energy increase and CO_2 reduction targets have been included in energy policy in Taiwan. Therefore, empirical electrical circuits modified with extra PV/VRB sources are utilized for the proposed NVC; the outcomes gained from this study validate the feasibility of the proposed novel voltage controller for running the reduction of carbon dioxide into synthetic fuels, and the comparison of two case solutions demonstrates the contribution of this letter, making it effective for electrochemical potential improvement in real applications. Another concrete benefit of both PEC and EC routes via the proposed NVC is better efficiency and yield of products utilizing Solar/BESS energy. The reliability of the scenario assessment becomes the major concern at this time. Further validation of this practical system will be reported in the near future.

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Conflicts of Interest: The author has no conflicts.

Appendix A

The parameters for the proposed NVC in Figure 6:

R-01~*R*-06 = 330 Ω, V*R*-01~*VR*-06 = 1 KΩ, SV*R*-1~*SVR*-6 = 200 Ω, C1~C3, C7, C9, C11, C13, C15, C17 = 22 µF, C4~C6, C7, C9, C11, C13, C15, C17 = 10 µF.

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